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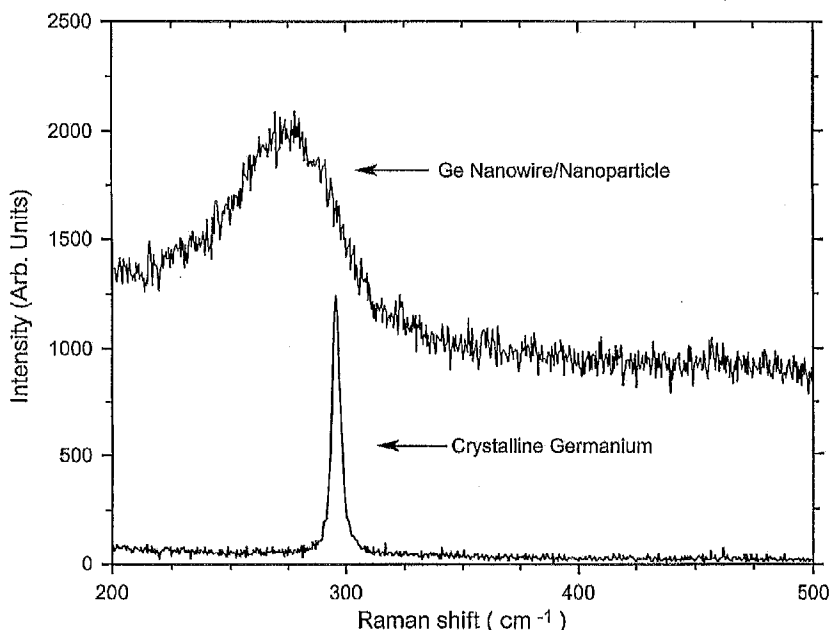
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CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: NANOSTRUCTURE-BASED HIGH ENERGY CAPACITY MATERIAL



(57) Abstract: A nanostructure based material is capable of accepting and reacting with an alkali metal such as lithium. The material exhibits a reversible capacity ranging from at least approximately 900mAh/g - 1,500mAh/g. The high capacity of the material makes it attractive for a number of applications, such as a battery electrode material.

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**Nanostructure-Based High Energy Capacity Material****STATEMENT REGARDING FEDERALLY SPONSORED  
RESEARCH OR DEVELOPMENT**

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At least some aspects of this invention were made with Government support under contract no. N00014-98-1-0597. The Government may have certain rights in this invention.

**BACKGROUND OF THE INVENTION**

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In the description that follows references are made to certain compounds, devices and methods. These references should not necessarily be construed as an admission that such compounds, devices and methods qualify as prior art under the applicable statutory provisions.

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With the increasing importance of batteries for a wide variety of uses, ranging from portable electronics to power supply devices for spacecraft, there is a long-felt need for new materials with higher energy densities.

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The energy density of a material can be quantified by measuring the amount of electron-donating atoms that can reversibly react with the material. One way of obtaining such a measurement is by setting up an electrochemical cell. The cell comprises a container housing an electrolyte, one electrode made of the electron-donating material (e.g. - an alkali metal), another electrode made of the material whose capacity is being measured (e.g. - a silicon nanostructure-based material), and an electrical circuit connected to the electrodes. Atoms of the electron-donating material undergo an oxidation reaction to form ions of the donating material, and free electrons. These ions are absorbed by the opposite electrode, and the free electrons travel through the electrical circuit. Since the number of electrons "given away" by each atom of the electron-donating material is known, by measuring the number of electrons transferred through the electrical circuit, the number of ions transferred to the material being investigated can be determined. This quantity is the specific capacity of the material, and can be expressed as milliampere-hours per gram of the material. For example, the maximum specific (reversible) capacity of graphite to accept lithium is reported to be approximately 372mAh/g. Because one lithium ion is transferred to the graphite electrode

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for every electron released, the specific capacity can be expressed in terms of the stoichiometry of the electrode material. For graphite, the saturation phase can be characterized as  $\text{LiC}_6$  with Li ions residing between the graphene layers. See, for example, (M. Winter et al., Insertion Electrode Materials for Rechargeable Lithium Batteries, Advanced Materials, Vol. 10, 10, "725-762", 1998; and J.R. Dahn et al., Mechanisms for Lithium Insertion in Carbonaceous Materials, *Science*, volume 270, October 27, 1995).

Lithium intercalated graphite and other carbonaceous materials are commercially used as electrodes for advanced Li-ion batteries. See, for example, M.S. Whittingham, editor, Recent Advances in rechargeable Li Batteries, *Solid State Ionics*, volumes 3 and 4, number 69, 1994; G. Pistoria, Lithium Batteries: New Materials, Development and Perspectives, *Elsevier*, 1994. The energy capacities of these conventional battery materials are partially limited by the  $\text{LiC}_6$  Li saturation concentration in graphite (equivalent to 372mAh/g).

In order to increase the capacities of electrode materials other carbon based-materials have attracted attention as potential electrode materials. Disordered carbon (soft and hard carbon) materials show reversible lithium storage capacities higher than that obtained from graphite (see, for example, J.R. Dahn et al., Mechanisms for Lithium Insertion in Carbonaceous Materials, *Science*, volume 270, October 27, 1995). Single wall carbon nanotube bundles have a large reversible Li storage capacity of 1000mAh/g, but at a large voltage hysteresis.

Lithium alloys have been investigated as possible anode materials for Li-based batteries. Si and Ge are known to form Li-rich alloys with compositions up to  $\text{Li}_{22}\text{Si}_5$  or  $\text{Li}_{22}\text{Ge}_5$ . They have been investigated for application in high temperature molten salt batteries (see, for example, R.N. Seefurth and R.A. Sharma, Investigation of lithium utilization from a lithium-silicon electrode, *J. Electrochem. Soc.*, Vol. 124, No. 8, 1207-1214, 1977). However, electrochemical reaction of Li with Si or Ge is only possible at high temperatures (higher than 350°C).

Pyrolysis of carbon and silicon-containing precursors has yielded materials with enhanced Li storage capacity (500-600mAh/g) (see, e.g., Carbonaceous materials containing silicon as anodes for lithium-ion cells, *Mat. Res. Soc. Proc.*, Vol. 393, page 305-313, 1995).

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It would be desirable to develop other materials having improved energy storage capacities and energy transfer properties. There exists a long-felt, but so far unfulfilled need, for a material having such properties. There exists a need for a material having improved properties that make it useful in battery electrodes and other high energy applications.

### SUMMARY OF THE INVENTION

These and other objects are attained according to the principles of the present invention.

One aspect of the present invention includes a material comprising a nanostructure that can reversibly react with foreign species. The material having a reversible capacity of at least 900mAh/g.

Another aspect of the present invention includes a material comprising silicon rod or wire-like nanostructures and intercalated lithium, the material having a reversible capacity of at least 900mAh/g.

A further aspect of the present invention includes a germanium-based material comprising a germanium and germanium oxide nanostructure. The material having a reversible capacity of at least 1000mAh/g.

In another aspect of the present invention, an article comprising an electrically conductive substrate, and a film deposited on the substrate which comprises any of the above-described materials. The article may take the form of an electrode for a battery.

### BRIEF DESCRIPTION OF THE DRAWING FIGURES

Figure 1 is a transmission electron microscope (TEM) micrograph of silicon nanostructures fabricated by a laser ablation method;

Figure 2 is a powder x-ray diffraction pattern of the silicon nanostructures used to store lithium.

Figure 3 is a Raman spectrum of the silicon nanostructures of the present invention;

Figure 4 is a Raman spectrum of the germanium nanostructures of the present invention;

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Figure 5 is a cross-sectional view of a nanostructure-coated substrate according to the present invention;

Figure 6 is an electrochemical cell incorporating an electrode material of the present invention;

5        Figure 7 is a graph showing the charge-discharge characteristics of a silicon nanostructure material formed according to the principles of the present invention;

Figure 8 shows the powder x-ray diffraction and Raman spectra collected from the electrode containing the silicon nanostructures at different stages of the first discharge cycle; and

10       Figure 9 is a graph showing the charge-discharge characteristics of a germanium nanostructure material formed according to the principles of the present invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15       A nanostructure-containing material can be formed by a number of techniques familiar to those skilled in the art, such as laser ablation of a target material, solution synthesis or chemical vapor deposition.

While the particular technique used to produce nanostructures is not essential to the practice of the present invention, a brief description of the production of such nanostructures is given below for purposes of illustration.

20       Numerous nanostructure materials are contemplated by the present invention. For example, nanostructures formed from silicon (Si), germanium (Ge) and aluminum (Al), silicon oxide and germanium oxide are specifically contemplated.

According to typical laser ablation techniques, a target is placed within a chamber. Preferably, the target contains a suitable catalyst such as iron (Fe) or gold (Au). The  
25       chamber is evacuated and then filled with inert gasses such as argon. The target is heated and then ablated with a suitable energy source such as a pulsed laser.

As the target is ablated, nanostructure-containing material is recovered from the vaporized target.

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The nanostructure materials formed according to the technique described above are generally either cage-like spherical particles or rod/wire shaped objects having nanometer-scale dimensions.

For example, silicon nanostructures may comprise rod or wire-like shapes having a diameter on the order of 1-50 nm and a length on the order of 0.5-10  $\mu\text{m}$ . Figure 1 is a TEM micrograph of silicon nanostructures formed by a laser ablation technique. Figure 2 is an x-ray diffraction pattern of these silicon nanostructures. The  $\text{FeSi}_2$  peaks are caused by the Fe catalysts present in the Si target. Moreover, the outer surfaces of the nanostructure objects are typically covered by thin layers of silicon oxides.

Nanostructures apparently have higher surface to volume ratio than the bulk material from which they are derived or from other forms of the material such as whiskers (see, for example, R.S. Wagner and W.C. Ellis in *Appl. Phys. Lett.*, Vol. 4, page 89, 1964 for the synthesis of Si whiskers).

The nanostructures are more reactive and may also have a lower melting temperature than the bulk materials. Therefore nanostructures formed of various materials such as Si, Ge, and Al exhibit increased reactivity and increased ability to reversibly react with alkali metals such as lithium.

For instance, Figure 3 illustrates another difference between bulk materials and nanostructures formed therefrom. As shown in Figure 3, the spectrum from bulk crystalline Si is compared with that of nanostructured Si. The characteristic Si  $\text{sp}^3$  stretching mode for nanostructured Si is slightly down-shifted from that of bulk crystalline Si.

One suitable technique for producing silicon nanostructures is described in A.M. Morales and C.M. Lieber, A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires, *Science*, 279, 208-211, 1998; and Y.F. Zhang and et al., Silicon nanowires prepared by laser ablation at high temperature, *Appl. Phys. Lett.*, 72, 15, 1835-1837, 1998.

Similarly, Figure 4 illustrates the characteristic Ge  $\text{sp}^3$  stretching mode of nanostructured Ge as being slightly down-shifted from that of the bulk crystalline Si.

Nanostructured Ge was synthesized using the laser ablation method (e.g.- Morales and Lieber, *Science* vol. 279, 208-211, 1998). Target composed of Ge and Fe (10atm.%)

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was ablated by a pulsed Nd:YAG laser at 900C under a constant flow of argon. Electron microscopy measurements show that thus synthesized materials comprise both Ge nanowires with an average diameter of 5-30nm and micron in length, and nanoparticles with the average diameter of 1-50nm.

5 Another advantage of the nanostructure materials of the present invention is that they can be rather easily deposited as a film onto a substrate material. For example, as illustrated in Figure 5, a sample of purified nanostructure material can be solution-deposited to form a coating 12 on an appropriate substrate.

10 Nanostructure-based materials of the present invention unexpectedly possess specific lithium storage capacities that exceed those possessed by conventional carbon-based materials.

As described in the Background, in a testing electrochemical cell, the lithium ions travel from the lithium electrode to the nanostructure material electrode during discharge. The lithium ions are readily accepted into the large surface area of the nanostructure material. When a lithium ion is accepted into the nanostructure material according to the present invention a chemical reaction takes place, even at temperatures on the order of 300°K and a distinct lithium-nanostructure material phase is formed, thus forming an "alloy" therewith. This reaction acts as a storage mechanism that enables the material to hold a charge (i.e.-in the form of lithium ions). As noted above, nanostructure materials exhibit increased reactivity. For example, while conventional macroscopic silicon must be heated to a temperature on the order of 400°C to react with lithium (see, for example, R.N. Seefurth and R.A. Sharma, Investigation of lithium utilization from a lithium-silicon electrode, *J. Electrochem. Soc.*, Vol. 124, No. 8, 1207-1214, 1977; C.J. Wen and R.A. Huggins, Chemical diffusion in intermediate phase in the lithium-silicon system, *J. of Solid State Chem.*, 37, 271-278 (1981).), the silicon nanostructure material of the present invention electrochemically reacts with lithium at room temperature or even lower.

The energy density, or ability of the silicon nanostructure material of the present invention to accept foreign species, such as alkali metals, and more specifically lithium, was measured by constructing a electrochemical cell, similar to that described in the Background



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section above. An electrochemical cell incorporating the silicon nanostructure-based material of the present invention is schematically illustrated in Figure 6.

A cell was constructed with a lithium foil electrode 20 and a stainless steel substrate plate 10 having a nanostructure film 12 deposited thereon, as the second electrode. A polypropylene filter soaked with an electrolyte 22 was placed between the two electrodes. Electrical contacts were made by two stainless steel plungers 24, 26 pressed against the electrodes. A current source 28 is connected to the plungers. The cell was then discharged and charged.

The nanostructure-lithium materials of the present invention have significantly higher capacities than conventional materials. For example, the silicon nanostructure-lithium materials of the present invention have exhibited capacities of 1500mAh/g in the first discharge cycle, reversible capacities on the order of at least 900mAh/g to at least approximately 1,000mAh/g and an irreversible capacity of less than 500mAh/g. Lithium discharge occurs at essentially a constant voltage below 0.1V. Most of the lithium can be removed from the nanostructured silicon electrode at below 0.5V.

Figure 7 is a voltage-capacity plot for a fully lithiated silicon nanostructure sample that showed a total capacity of approximately 1300mAh/g. The reversible part, defined as the capacity displayed after the second discharge, is approximately 800mAh/g. The inset of Figure 7 illustrates the capacity of the material versus the number of charge-discharge cycles. Figure 8 illustrates x-ray diffraction and Raman spectrum data collected from a Si nanostructure electrode at different stages of the first discharge cycle.

The x-ray and Raman intensities from the nanostructured Si decreases with increasing Li concentration and vanished in the fully lithiated state (spectra a, b and c). The characteristic Si  $sp^3$  stretching mode re-appeared in the Raman spectrum in the electrode at the end of the first charge (spectrum d), indicating recovery of  $sp^3$  Si after extraction of Li. Inset shows the voltage versus capacity data from the same cell and the integrated x-ray intensity ratio of the Si (111) and FeSi<sub>2</sub> peaks (FeSi<sub>2</sub> is inert to Li and is used as the internal reference).

Figure 9 illustrates the second-cycle charge-discharge data from a sample containing nanostructured Ge and Ge oxide, after vacuum annealing at 150°C. The data were collected

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under galvanostatic mode using 50mA/g rate at 300K. The reversible Li capacity is 1500mAh/g (normalized with the total sample weight, the value will be higher than the total capacity is normalized with weight of nanostructured Ge, excluding the Fe catalysts). A distinct voltage step is present during both Li insertion and extraction.

5           Another important performance parameter is how the rate of charging and discharging affects the capacity of the material. Some applications, such as electrical vehicles, require the electrode material to operate under high rate charging and discharging conditions. Generally, the capacity of the material decreases with an increased rate. The nanostructure-lithium material of the present invention exhibits high capacities, even when  
10 charged/discharged at high rates.

          Yet another important performance parameter is the electrochemical potential with respect to Li. For example, lithium insertion into the current Si nanostructure based material occurs below 0.1V and lithium extraction takes place mostly below 0.5V. This means that the nanostructured silicon based materials can replace the current carbon based negative  
15 electrodes in the Li-Ion batteries without reduction in the cell voltage.

          According to the present invention, it is also possible to further increase the Li storage capabilities of the nanostructure materials through addition processing of the material. For example, nanostructured Si samples from the same batch were annealed at different temperatures (200-900C) under  $5 \times 10^{-6}$  torr vacuum. Their charge/discharge  
20 characteristics were measured under the same conditions as described above. The total discharge and reversible Li capacities were found to initially increase with the annealing temperature up to ~600C then decrease with further increase of the annealing temperature. Annealing is believed to remove chemical species on the surfaces of nanostructured Si. These chemical species and oxide coating can also be removed by other processes such as  
25 hydrogen plasma.

          The excellent capacity of the nanostructure-based materials of the present invention, combined with their superb mechanical and electrical properties, and the ease of forming films, make them attractive electrode materials for high energy density batteries (e.g.-high energy density Li-ion batteries), batteries for high current rate applications, and thin-film  
30 batteries.

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Although the present invention has been described by reference to particular embodiments, it is in no way limited thereby. To the contrary, modifications and variants will be apparent to those skilled in the art in the context of the following claims.

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WHAT IS CLAIMED IS:

1. A material comprising a nanostructure and a foreign species, said material having a reversible capacity of at least 900 mAh/g.

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2. The material of claim 1, wherein the material is silicon-based and comprises silicon nanostructures.

3. The material of claim 1, wherein said nanostructure comprises at least one of a rod, wire-like shape, or spherical particles.

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4. The material of claim 3, wherein the rod or wire-like shape has a diameter of about 1-50nm and a length of about 0.5-10 $\mu$ m.

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5. The material of claim 1, wherein the foreign species comprises alkali metal.

6. The material of claim 5, wherein the alkali metal comprises lithium.

7. The material of claim 1, wherein the reversible capacity is at least 1,000mAh/g.

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8. The material of claim 7, wherein the material is germanium-based and comprises germanium nanostructures.

9. The material of claim 1, further comprising an irreversible capacity of less than approximately 500mAh/g.

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10. A material comprising at least one of germanium and silicon nanostructures, said material having a reversible capacity of at least 900mAh/g.

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11. The material of claim 10, wherein the material has a reversible capacity of at least 1,000mAh/g.

12. The material of claim 10, wherein the material has an irreversible capacity of  
5 less than 200mAh/g.

13. An article of manufacture comprising:  
an electrically conductive substrate; and  
a film disposed on said substrate, said film comprising the material of claim  
10 10.

14. The article of claim 13, wherein said substrate comprises an electrically  
conductive metal.

15 15. The article of claim 13, wherein said article comprises an electrode.

16. A germanium-based material and a foreign species comprising a germanium  
and germanium oxide nanostructure and a foreign species, said material having a reversible  
capacity of at least 1,000 mAh/g.

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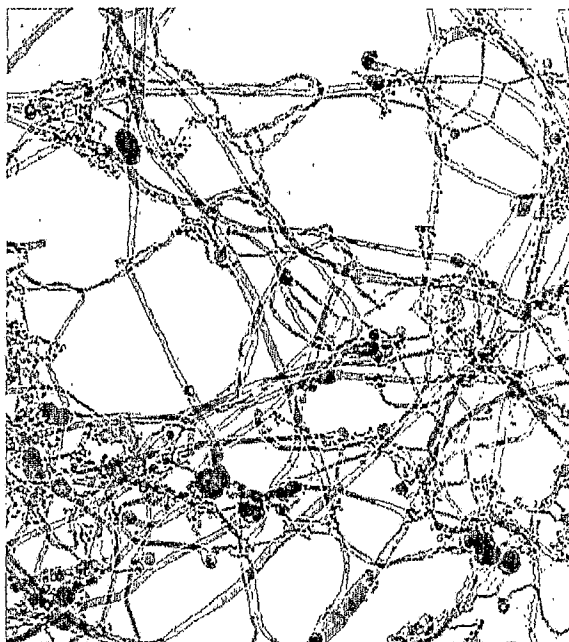


FIG. 1

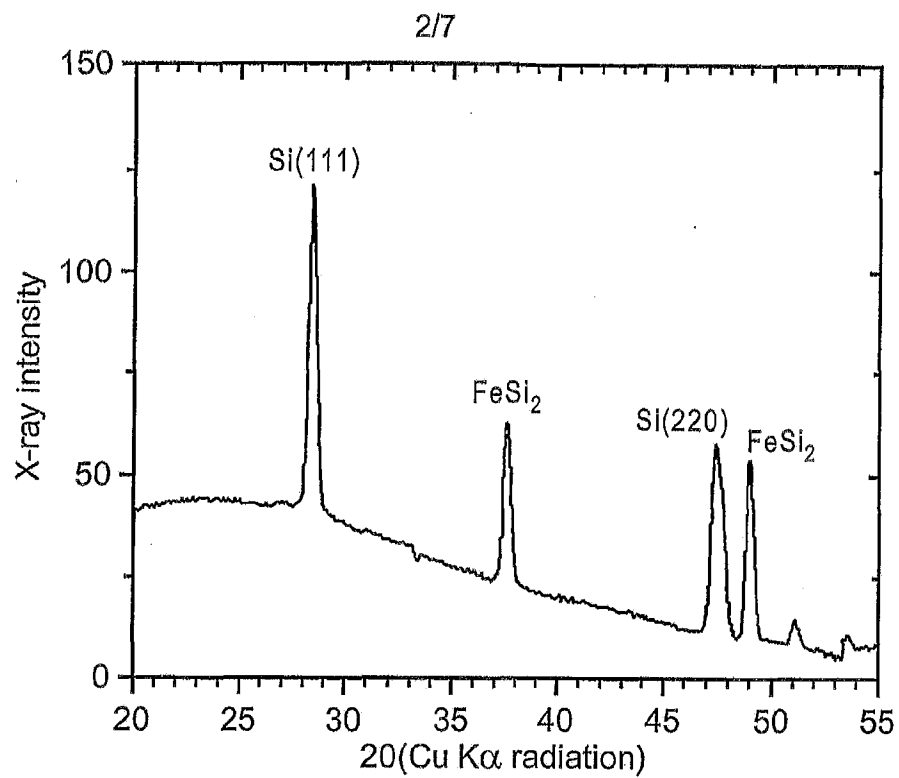


FIG. 2

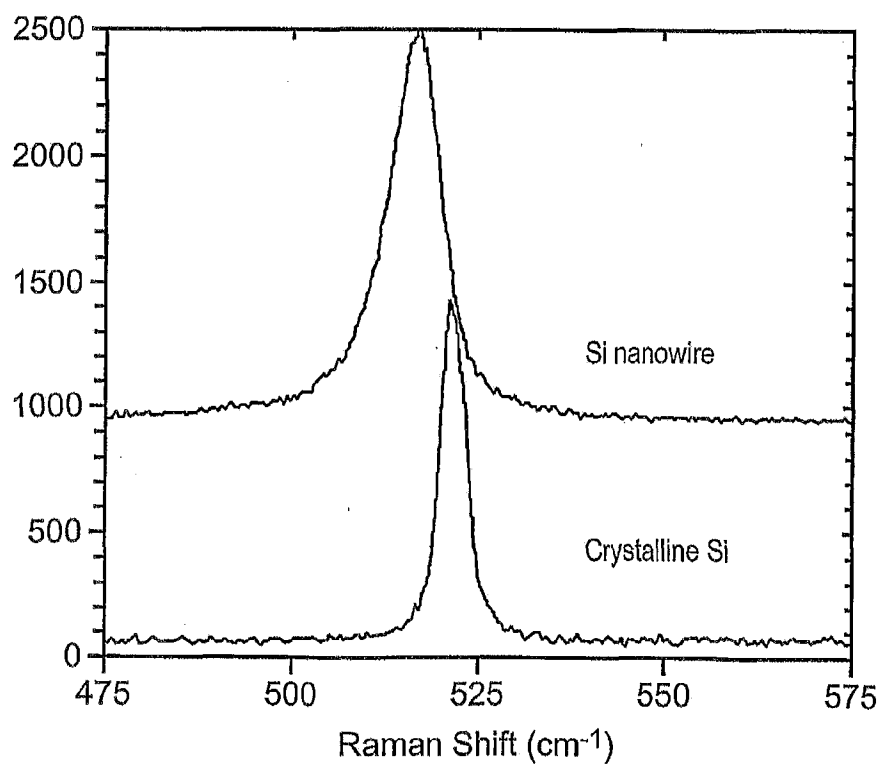


FIG. 3

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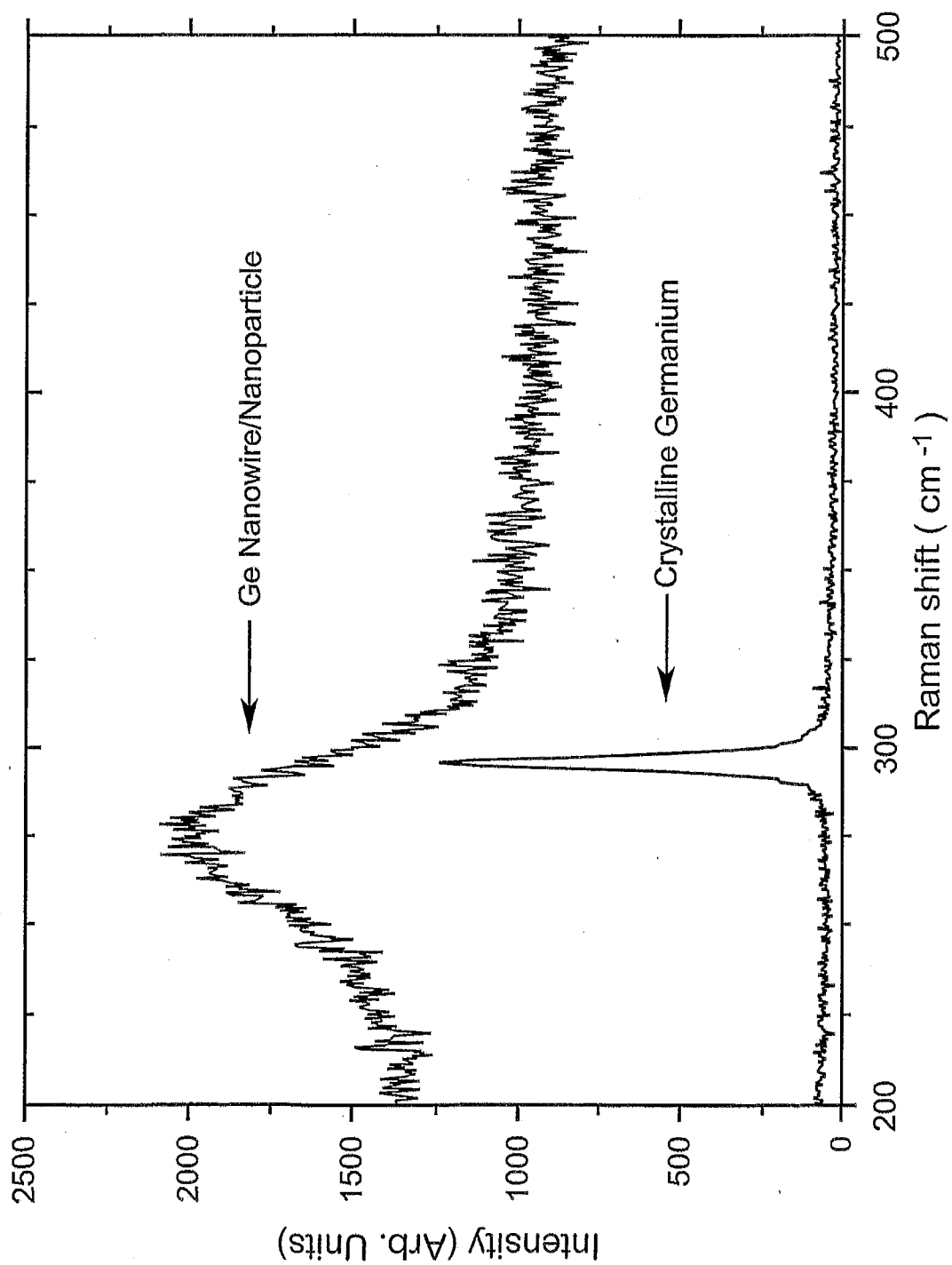


FIG. 4



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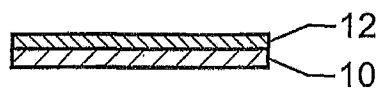


FIG. 5

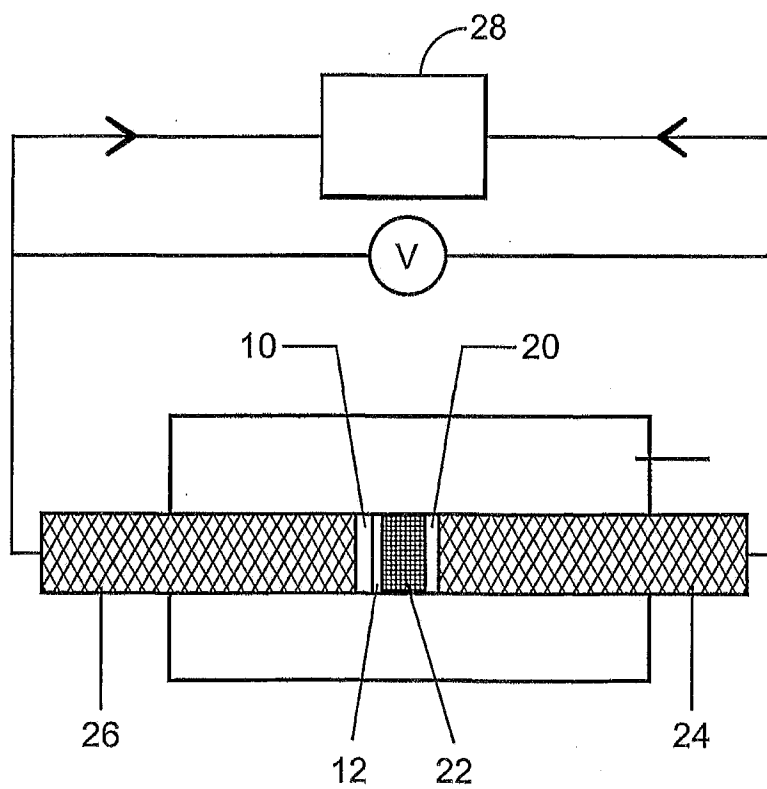


FIG. 6

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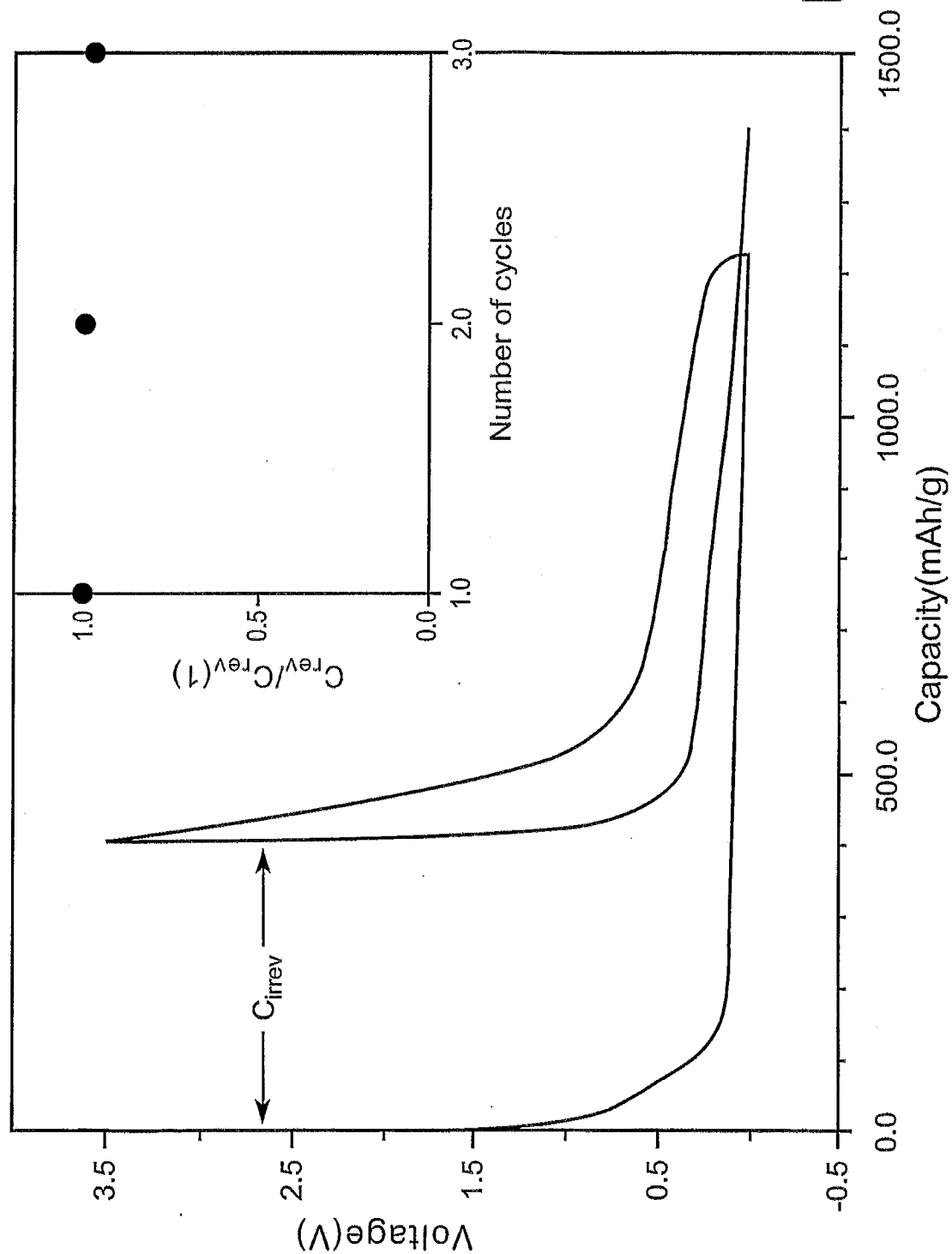
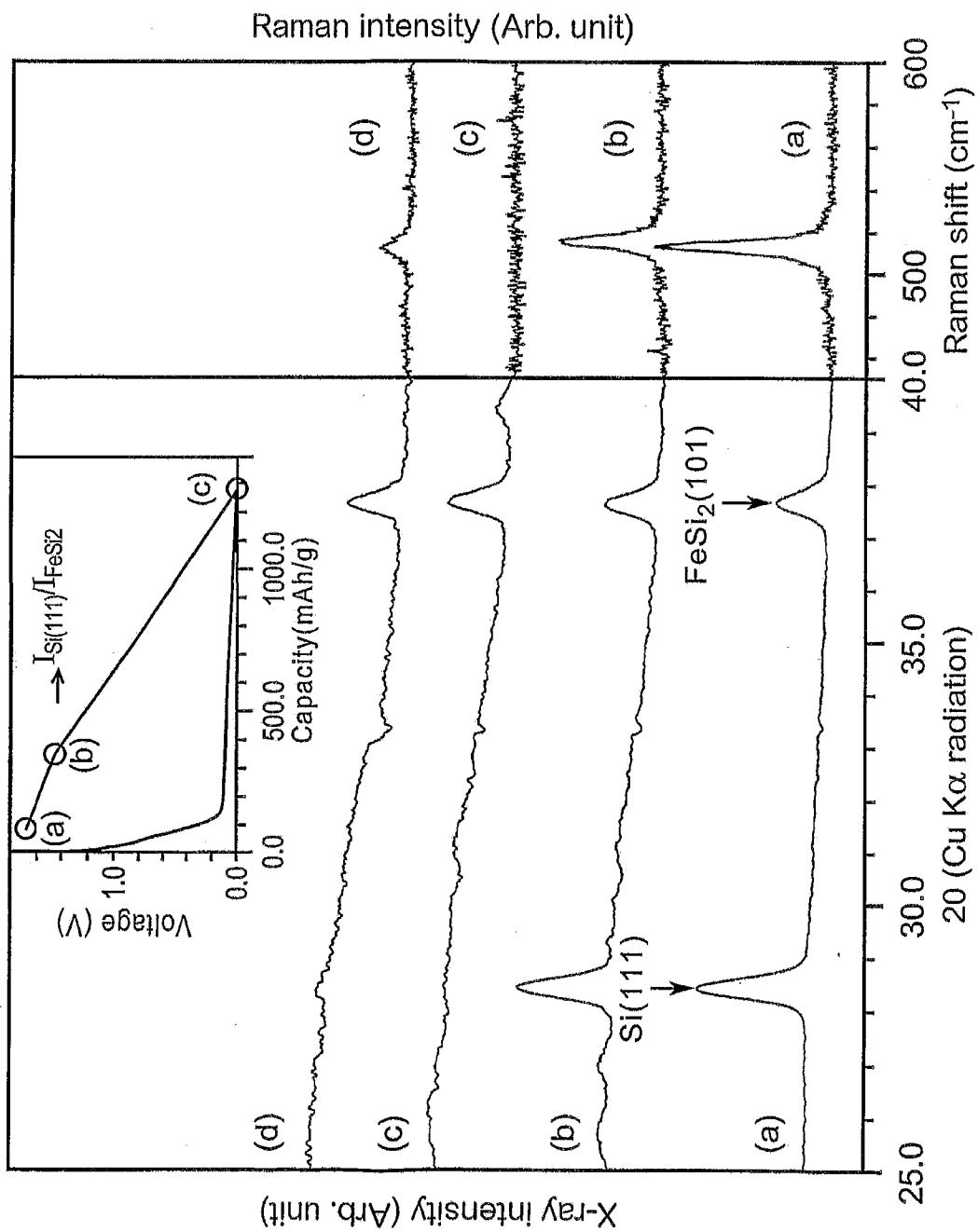


FIG. 7

FIG. 8



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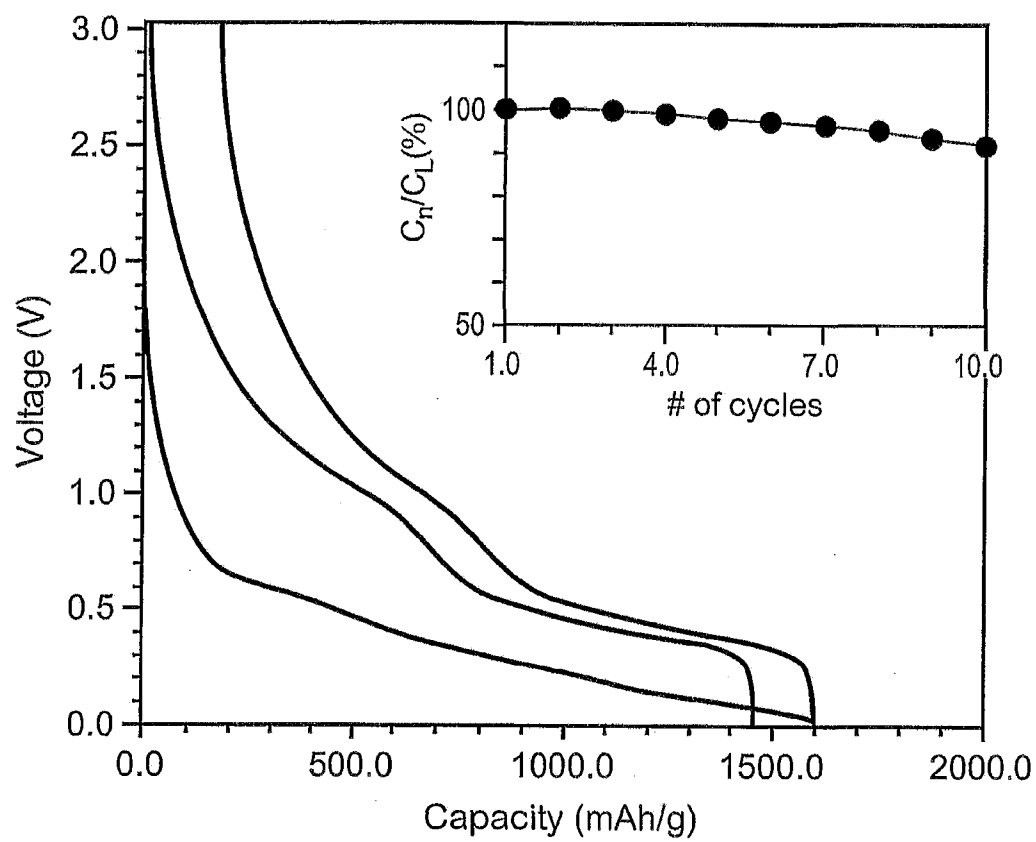


FIG. 9

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/18846

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 27/26; H01L 29/41, 29/43; D01F 9/12; C01B 31/30

US CL : 204/409, 410, 421; 428/345, 346; 257/741, 742

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/409, 410, 421; 428/345, 346; 257/741, 742

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,997,832 A (LIEBER et al) 7 December 1999, col. 4, lines 34-36, lines 50-54, col. 3 lines 24-30, lines 50-58, col. 5 line 19.	1-9, 10-12
Y	US 5,457,343 A (AJAYAN et al) 10 October 1995, col. 3, lines 22-26 & 34, col. 6 line 12.	1-16
A	US 5,338,430 A (PARSONAGE et al) 16 August 1994, Abstract	
A	US 5,587,256A (WILSON et al) December 1996.	
X	G. W. ZHOU et al, "Controlled Li doping of Si nanowires by electrochemical insertion method", Applied Physics Letters, Vol 75, No. 16, October 18, 1999, page 2447-2449.	1-3, 5-7, 10-11, 17

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	J. R. Dahn, "Mechanisms for Lithium Insertion in Carbonaceous Materials", Science, Vol. 270, October 27, 1995, page 590-593.	
A	R. N. Seefurth et al., "Investigation of Lithium Utilization from A Lithium-Silicon Electrode", J. Electrochem Soc., Vol. 124, No. 8, August 1977, page 1207-1214.	
A	A. M. Morales et al., "A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires", Science, Vol. 279, January 9, 1998, page 208-211.	
A	Y. F. Zhang et al., "Silicon nanowires prepared by laser ablation at high temperature", Applied Physics Letters, Vol. 72, No. 15, April 13th, 1998, page 1835-1837.	
A	C. John Wen et al., "Chemical diffusion in Intermediate phases in the Lithium-Silicon System", Journal of Solid State Chemistry, Vol. 37, 1981, page 271-278.	
A	M. Winter et al., "Insertion Electrode Materials for Rechargeable Lithium Batteries" Advanced Materials, Vol. 10, 1998, page 725-262.	
A	M. S. Whittingham (Editor), "Recent Advances in Rechargeable Li Batteries" Solid state Ionics, Vol. 69, No. 3, 4, 1994.	
A	G. Pistoia (Editor), "Lithium Batteries: New Materials, Developments and Perspectives", Industrial Chemistry Library, Vol. 5, Elsevier, 1994.	
A	A. M. Wilson et al., "Carbonaceous Materials Containing Silicon as Anodes for Lithium-ion Cells" Mat. res. Soc. proc., Vol. 393, 1995, page 305-313.	

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOSHIBA CORP

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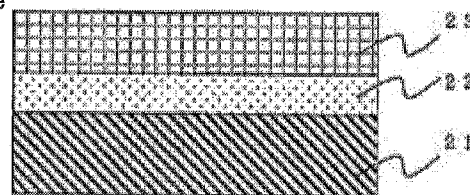
(72)Inventor : KONO RYUKO  
TAKAMI NORIO

## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a lithium ion secondary battery with good cycle characteristic by preventing a negative active material from turning into fine particles and from desorbing when a metal active material is used as a negative active material.

**SOLUTION:** With a lithium ion secondary battery consisting of a positive electrode, a negative electrode and a separator pinched by both electrodes, a laminated body laminated with a collector 21, a negative active material layer 22 and a coating layer 23 made of carbon material in turn is used as a negative electrode.



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**CLAIMS**

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[Claim(s)]

[Claim 1]An anode which is formed in a cathode which possesses positive active material at least, a charge collector, and this collector surface, and possesses an enveloping layer which consists an alkaline metal of a carbon material formed on a negative electrode active material layer which has occlusion and an alloy to emit, and this negative electrode active material layer, A nonaqueous electrolyte secondary battery having the nonaqueous electrolyte inserted into said cathode and an anode.

[Claim 2]The nonaqueous electrolyte secondary battery according to claim 1, wherein thickness of said active material layer is 0.01 micrometers or more 50 micrometers or less.

[Claim 3]The nonaqueous electrolyte secondary battery according to claim 1, wherein thickness of said enveloping layer is 0.1 micrometers or more 200 micrometers or less.

[Claim 4]The nonaqueous electrolyte secondary battery according to claim 1, wherein a film parameter of a negative electrode active material layer to thickness of said enveloping layer is 0.95 or less [ 0.01 or more ].

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[Translation done.]



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a nonaqueous electrolyte secondary battery and its electrode.

[0002]

[Description of the Prior Art]In recent years, highly efficient-ization to the rechargeable battery which is a power supply of these electronic devices is demanded with the miniaturizations of an electronic device and increases of demand, such as a cellular phone and a portable personal computer. As this rechargeable battery, the nonaqueous electrolyte battery used for the negative pole material is developed [ substance / occlusion and / which can be emitted ] in lithium like a carbon material, and it has spread as a power supply for portable electronic apparatus. Unlike the conventional cell, this nonaqueous electrolyte secondary battery has the feature of it being lightweight and having 4V class high electromotive force, and that outstanding performance attracts attention.

[0003]Then, applying said nonaqueous electrolyte secondary battery as a power supply of an electromobile, a power tool, a cordless cleaner, etc., etc. is examined. In such a use, to high-energy-density-ize more is demanded compared with the conventional nonaqueous electrolyte secondary battery.

[0004]The nonaqueous electrolyte secondary battery which used a lithium metal, a lithium alloy, etc. for the active material of the electrode is expected as a high energy cell, and research and development are furthered briskly.

[0005]As positive active material, although  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc. are put in practical use, The lithium ion battery using occlusion and the carbon material to emit as negative electrode active material is widely put in practical use in lithium, and the rechargeable battery which used the lithium metal and the lithium alloy for the anode is not yet put in practical use.

[0006]The Reason the lithium metal is not put in practical use has the problem that an internal short circuit and a cycle life are short, in order that disconnection by generating of lithium of the shape of a dendrite by degradation of lithium by the reaction of nonaqueous electrolyte and a lithium alloy and repetition of charge and discharge (arborescence) may occur. In order to solve such a problem, the research which alloys lithium and is used for negative electrode active material was made. For example, so that a part of aluminum may be used, although there are technology etc. which use a lithium aluminum alloy etc. as an anode (for example, J. O. BesenHard, J. Electroanal. Chem., 94, 77. (1978)), Under charge and discharge with shallow fixed quantity of electricity, efficiency is improvable. However, if deep charge and discharge are repeated, by the volume change of an electrode, negative electrode active material will carry out pulverization, and some negative electrode active material will disconnect itself of an anode too. As a result, since the amount of negative electrode active material in an anode decreased gradually, there was a problem in a charge-discharge cycle characteristic.

[0007]Although the copper-tin alloy, alloys, for example, a tin-nickel alloy, other than a lithium alloy, etc. are studied as negative electrode active material for attaining a high energy cell, since the same Reason problem as a lithium alloy arises, it has not resulted in utilization.

[0008]

[Problem to be solved by the invention]As mentioned above, in the conventional nonaqueous electrolyte secondary battery, there was a problem that the cycle characteristic of what can raise an energy density if a metallic material is used as negative electrode active material fell.

[0009]In view of such a problem, it succeeds in this invention, and it is a thing.

\*\* of the purpose is high and it is providing the nonaqueous electrolyte secondary battery excellent in charge-and-discharge cycle performance.

[0010]

[Means for solving problem]This invention is characterized by a nonaqueous electrolyte secondary battery comprising the following.

The cathode which possesses positive active material at least.

The anode possessing the enveloping layer which is formed in a charge collector and this collector surface, and consists an alkaline metal of a carbon material formed on the negative electrode active material layer which has occlusion and an alloy to emit, and this negative electrode active material layer. Nonaqueous electrolyte inserted into said cathode and the anode.

[0011]Although the negative electrode active material layer which consists of alloys is used for the nonaqueous electrolyte secondary battery of this invention, Since it is held by the enveloping layer in an electrode even if negative electrode active material atomizes, as a result of controlling atomization of an alloy by forming an enveloping layer in the negative electrode active material layer surface and carrying out by repeating the charge and discharge of a cell, it becomes possible to control reduction in negative electrode active material.

[0012]Since a carbon material which can pass alkaline metals, such as lithium, is used as an enveloping layer, negative electrode active material does not become hindrance about an alkaline metal, when emitting, occlusion and. Since it has occlusion and discharge ability of the carbon material [ itself ] alkaline metal, compared with a case where it covers with other materials, a fall of an energy density by an enveloping layer can be suppressed.

[0013]As for thickness of said active material layer, it is preferred that it is [ 0.01 micrometer or more ] 50 micrometers or less.

[0014]As for the from film of said enveloping layer, it is preferred that it is [ 0.1 micrometer or more ] 200 micrometers or less.

[0015]As for a film parameter of a negative electrode active material layer to thickness of said enveloping layer, it is preferred that it is [ or more 0.01 ] 0.95 or less.

[0016]Although a ratio of a negative electrode active material layer can be improved and occlusion and discharge ability of an alkaline metal of negative electrode active material can be raised by reducing a ratio of an enveloping layer, when thickness of an enveloping layer is too small, there is a possibility that it may become impossible to hold negative electrode active material. When thickness of an enveloping layer is large, there is a possibility of making low permeability to negative electrode active material of an alkaline metal.

[0017]

[Mode for carrying out the invention]Drawing 1 is a top view about a left half plane of a cylindrical nonaqueous electrolyte secondary battery, shows a right half plane with drawing of longitudinal section, and explains it with reference to Drawings below.

[0018]As for the container 1 of closed-end cylindrical shape which consists of metal, for example, stainless steel, the insulator 12 is arranged at the pars basilaris ossis occipitalis. This electrode group 3 is stored in said container 1. Said electrode group 3 has structure which whirled so that said anode 6 might be located outside, and wound upwards the band-like thing which laminated the cathode 4, the separator 5, the anode 6, and another separator 5 in this order. Said separator 5 is formed, for example from a nonwoven fabric, polypropylene microporous film, polyethylene microporous film, and a polyethylene polypropylene fine porosity laminated film. An electrolysis solution permeates into the separator 5 because an electrolysis solution accommodates in said container 1.

[0019]Caulking immobilization of the positive pole terminal 9 of the hat form arranged at the safety valve 8 arranged on PTC element 7 to which the opening of the hole was carried out in the center section, and said PTC element 7, and said safety valve 8 is carried out via the insulating gasket 10 at the upper opening of said container 1. One end of the collecting lead 11 for cathodes is connected to said cathode 4, and the other end is connected to said positive pole terminal 9, respectively. Said anode 6 is connected to said container 1 which is a negative pole terminal via the collecting lead 13 for anodes.

[0020]In the nonaqueous electrolyte secondary battery concerning this invention, they may be an electrode group which has the structure where the laminated material in which a sheathing material consists of laminate films, and consists of said cathode and an anode, and a separator in said sheathing material was wound around flat state, and the structure where nonaqueous electrolyte was stored.

[0021]Next, said cathode 4, said separator 5, said anode 6, and said nonaqueous electrolyte are explained in detail.

[0022]1) Cathode 4 cathode contains positive active material at least, forms a positive active material layer in sheet shaped one side or both sides of a charge collector, and usually uses it for them. For example, what is necessary is to apply the suspended solid suitably suspended to the solvent, to dry, to press positive active material, a conducting agent, and a binding agent in the collector surface of aluminium foil etc., and just to form a positive active material layer in it.

[0023]Positive active material carries out occlusion of the alkaline metal at the time of discharge of a cell, and it can be used for it, without being limited especially if an alkaline metal can be emitted at the time of charge.

[0024]For example, various oxides and a sulfide are mentioned as positive active material used for the rechargeable lithium-ion battery using lithium as an alkaline metal. For example, manganese dioxide ( $\text{MnO}_2$ ), a lithium manganese multiple oxide (for example,  $\text{LiMn}_2\text{O}_4$  or  $\text{LiMnO}_2$ ), Lithium nickel complex oxide (for example,

$\text{LiNiO}_2$ ), a lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ), a lithium nickel cobalt multiple oxide (for example,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ), a lithium manganese cobalt multiple oxide (for example,  $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ ), and vanadium oxide (for example,  $\text{V}_2\text{O}_5$ ) etc. — it is mentioned. Organic materials, such as conductive polymer material and a disulfide system polymeric material, are also mentioned. The lithium manganese multiple oxide whose cell voltage of more desirable positive active material is high ( $\text{LiMn}_2\text{O}_4$ ), Lithium nickel complex oxide ( $\text{LiNiO}_2$ ), a lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ), A lithium nickel cobalt multiple oxide ( $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ), a lithium manganese cobalt multiple oxide ( $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ ), etc. are mentioned.

[0025]As a charge collector, although it can be used without being restricted especially if it is a conductive material, it is preferred to use especially material which cannot oxidize easily at the time of a cell reaction as a charge collector for cathodes, for example, it should just use aluminum, stainless steel, titanium, etc.

[0026]As said conducting agent, acetylene black, carbon black, black lead, etc. can be mentioned, for example. As said binding agent, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), fluorine system rubber, etc. are mentioned, for example. As for a compounding ratio of said positive active material, a conducting agent, and a binding agent, it is preferred to use the range of 80 to 95 weight % of positive active material, 3 to 20 weight % of conducting agents, and 2 to 7 weight % of binding agents.

[0027]2) A sectional view showing an example of an anode concerning this invention is shown in anode 6 drawing 2.

[0028]The anode 6 concerning this invention is provided with the following.

The charge collector 21.

The negative electrode active material layer 22 which is formed in a collector surface and contains negative electrode active material at least.

The enveloping layer 23 which consists of a carbon material formed on this negative electrode active material layer.

[0029]If the charge collector 21 is a conductive material, it can be especially used without restriction, but as a charge collector for anodes, using material which is hard to dissolve at the time of a cell reaction should just use sheet shaped copper, nickel, etc. preferably especially.

[0030]The negative electrode active material layer 22 carries out the stratification of the mixture containing a negative-electrode-active-material independent or negative electrode active material. It is a metallic material which emits an alkaline metal at the time of discharge of a cell, and can carry out occlusion of the alkaline metal as this negative electrode active material at the time of charge. For example, in a rechargeable lithium-ion battery using lithium as an alkaline metal, For example, Sn-Ni alloy, a Sn-nickel-Cu alloy, a Sn-Sb alloy, Cu-Sn alloy, Lithium alloys, such as a Sn-Sb-Cu Al alloy, Mg-Sn alloy, a Mg-Sb alloy, a Mg-Sb-Ni alloy, Li-aluminum alloy, a Li-Pb alloy, a Li-In alloy, a lithium metal, etc. can be mentioned. Especially the alloy containing lithium can raise charge and discharge efficiency remarkably. As for a desirable range, it is preferred less than more than 0.02wt%55wt% and to use especially less than 0 and more than 05wt%45wt%, and an alloy which contains lithium not more than more than 0.1wt%30wt% still more desirably preferably.

[0031]Especially a crystal structure of a negative electrode active material layer formed by doing in this way may be a crystal phase, micro crystallite, or an amorphous phase, without being limited. What is necessary is to form a single phase by the material system, to consider it as an alloy which consists of two or more phases, or just to adjust if needed, when negative electrode active material is an alloy. Although various impurities, such as fluorine, may mix into negative electrode active material, if each impurity quantity is less than 1wt%, a function as negative electrode active material can usually fully be exhibited.

[0032]As for thickness of the negative electrode active material layer 22, it is preferred that they are 0.01–50 micrometers and 0.05 more micrometer – 30 micrometers, and it is preferred to use 0.1 micrometer – 15 micrometers especially. Since a lithium ion occlusion amount of an anode will become small if smaller than a range which thickness mentioned above, cell capacity will become small. If larger than a range mentioned above, negative electrode active material atomizes, and there is a possibility of disconnecting oneself of a negative electrode active material layer.

[0033]The negative electrode active material layer 22 can be formed in a collector surface using a known method, for example, a sintering process, rapid quenching, the plating method, a sputtering method, the rolling method, a sol gel process, vacuum deposition, etc.

[0034]For example, moving an alloy which consists of negative electrode active material adjusted to predetermined composition ratio arranged on a charge collector in the range of the movement speed 5 – 50 m/s. A stratified quenching object which becomes a collector surface from negative electrode active material can be created by quenching with the hyperquenching equipment using the single rolling method or the congruence rolling method. A negative electrode active material layer can be formed in a collector surface by carrying out pressing of the powder of each element which constitutes negative electrode active material to a

charge collector and one, and heat-treating it under an inert gas atmosphere or a vacuum after that.

[0035]It may heat-treat further if needed to the negative electrode active material layer 22 formed by these methods. Although this treatment temperature is influenced with the constituent of the negative electrode active material layer 22, it is preferred to carry out in a temperature requirement (about 100 °C – about 500 °C). Although the optimal heat treating time is changed with heat treatment temperature, 1 to 50 hours is more preferably good preferably as a rule of thumb for 0.5 to 100 hours for 0.1 to 500 hours.

[0036]The enveloping layer 23 is formed on a negative electrode active material layer, control the volume change of a negative electrode active material layer, and atomization is controlled, and also when it atomizes, it functions as covering for holding this particle on a charge collector. By forming this enveloping layer, it becomes possible to control the cubical expansion of a negative electrode active material layer, and fine complications-ization can be prevented.

[0037]It forms of ingredients, such as a carbon material conventionally used as negative electrode active material as the enveloping layer 23, or this carbon material, binding resin. As a carbon material, graphite, acetylene black, carbon black, etc. are specifically mentioned.

[0038]Since passage of a lithium ion is possible for this enveloping layer 23, it does not bar the occlusion and discharge of the lithium elements to the positive active material layer 22 by the enveloping layer 23. Since it also has a function as negative electrode active material as mentioned above, the lithium occlusion amount of an anode can be raised compared with the case where other materials are used. If a conducting agent is furthermore added in the enveloping layer 23, it will become possible to raise the collecting efficiency in the inside of coating membrane.

[0039]Thickness of the enveloping layer 23 has preferred 0.1-micrometer or more thing set to 200 micrometers or less. If thinner than 0.1 micrometer, it is difficult to form a uniform film, and if it exceeds 200 micrometers, the permeability of a lithium ion will fall. A film parameter of the negative electrode active material layer 22 to thickness of the enveloping layer 23 has preferred or more 0.01 thing to do to 0.95 or less. If it becomes difficult to fully control disconnection in a negative electrode active material layer if smaller than 0.01 and it exceeds 0.95, a ratio of negative electrode active material will decrease, and there is a possibility that an occlusion amount of lithium may fall.

[0040]For example, the enveloping layer 23 is created as follows.

[0041]Although the enveloping layer 23 should just contain negative electrode active material at least, it consists of conducting agents a carbon material, a binding agent, and if needed, and is formed by carrying out spreading / dry press of the suspension which suspended these ingredients to a suitable solvent via a negative electrode active material layer on the charge collector 21.

[0042]As said binding agent, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), fluorine system rubber, ethylene-butadiene rubber (SBR), carboxymethyl cellulose (CMC), etc. are mentioned, for example.

[0043]About a solvent used when forming the enveloping layer 22, when the negative electrode active material layer 22 reacts to water easily, it is desirable to use a suitable organic solvent, for example, N-methyl-pyrrolidone (NMP) solution. As for a compounding ratio of said negative electrode active material, a conducting agent, and a binding agent, it is preferred to use the range of 70 to 95 weight % of negative electrode active material, 0 to 25 weight % of conducting agents, and 2 to 10 weight % of binding agents.

[0044]A negative electrode active material layer and an enveloping layer can be formed in sheet shaped one side or both sides of a charge collector.

[0045]3) The separator 5 aforementioned separator 5 holds the nonaqueous electrolyte concerning this invention, and. It is for insulating between a cathode and an anode, and it can consist of an insulating material, and can be used, without being limited especially if it has fine pores which connect between a cathode and an anode, and the nonwoven fabric made of a synthetic resin, a polyethylene porosity film, a polypropylene porosity film, etc. can specifically be mentioned.

[0046]4) The liquid electrolyte prepared when the nonaqueous electrolyte held at the nonaqueous electrolyte separator 5 dissolves an electrolyte in a nonaqueous solvent. Or the polymer gel electrolyte containing said nonaqueous solvent and said electrolyte, the solid polymer electrolyte only containing said electrolyte, and the inorganic solid electrolyte that has lithium ion conductivity are mentioned to a polymer material.

[0047]As a liquid electrolyte, it is what dissolved lithium salt, for example in the nonaqueous solvent of the lithium cell as an electrolyte, and a publicly known nonaqueous solvent can be used, It is more preferred than cyclic carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), and cyclic carbonate and cyclic carbonate to use the nonaqueous solvent which makes a subject a mixed solvent with the nonaqueous solvent (the following 2nd solvent) of hypoviscosity.

[0048]As the 2nd solvent, for example Dimethyl carbonate, methylethyl carbonate, Chain carbonate, such as diethyl carbonate, gamma-butyrolactone, Dimethoxyethane, diethoxyethane, etc. are mentioned as chain ether, such as a tetrahydrofuran and 2-methyltetrahydrofuran, as acetonitrile, methyl propionate, ethyl propionate, and cyclic ether.

[0049]As an electrolyte, although alkali salt is mentioned, especially lithium salt is mentioned. As lithium salt,

lithium hexafluorophosphate ( $\text{LiPF}_6$ ), lithium borofluoride ( $\text{LiBF}_4$ ), Arsenic lithium hexafluoride ( $\text{LiAsF}_6$ ), lithium perchlorate ( $\text{LiClO}_4$ ), trifluoro meta-sulfonic acid lithium ( $\text{LiCF}_3\text{SO}_3$ ), etc. are mentioned. In particular, lithium hexafluorophosphate ( $\text{LiPF}_6$ ) and lithium borofluoride ( $\text{LiBF}_4$ ) are preferred. As for the dissolved amount to said nonaqueous solvent of said electrolyte, it is preferred to carry out in 1. and 0.5–2.0 mol /.

[0050]It is what dissolved said solvent and said electrolyte in the polymer material as a polymer gel electrolyte, and was made into gel. As a polymer material, the polymer of monomers, such as polyacrylonitrile, polyacrylate, polyvinylidene fluoride (PVdF), and polyethylene oxide (PECO), or a copolymer with other monomers is mentioned.

[0051]As a solid electrolyte, it dissolves in a polymer material and said electrolyte is solidified. As a polymer material, the polymer of monomers, such as polyacrylonitrile, polyvinylidene fluoride (PVdF), and polyethylene oxide (PEO), or a copolymer with other monomers is mentioned. The charge of a ceramic material containing lithium is mentioned as an inorganic solid electrolyte, and  $\text{Li}_3\text{N}$ ,  $\text{Li}_3\text{PO}_4\text{--Li}_2\text{S--SiS}_2$ , and  $\text{LiI--Li}_2\text{S--SiS}_2$  glass etc. are mentioned especially.

[0052]In drawing 1 mentioned above, although the example applied to the cylindrical shape nonaqueous electrolyte secondary battery was explained, it is applicable also like a square-shaped nonaqueous electrolyte secondary battery. The electrode group stored by the container of said cell may make not only a spiral type but a cathode, a separator, and an anode the form which carried out plural laminates in this order.

[0053]If the nonaqueous electrolyte secondary battery concerning this invention is in the range of this invention, it will not be limited to the form mentioned above.

[0054]

[Working example]The nonaqueous electrolyte secondary battery as shown in drawing 1 was created.

[0055]<production of a cathode> — first 91 weight % of lithium cobalt oxide ( $\text{LiCoO}_2$ ) powder of positive active material with 2.5 weight % of acetylene black, 3 weight % of graphite, and 4 weight % of polyvinylidene fluorides (PVdF). N-methyl-pyrrolidone (NMP) solution was added, and it mixed, and applied to the charge collector of 15-micrometer-thick aluminium foil, and the cathode of electrode density  $3.0 \text{ g/cm}^3$  was produced by pressing after desiccation.

[0056]<production of an anode> — first, on the charge collector which consists of 12-micrometer-thick copper foil, plating of the alloy thin film which consists of presentation 0.75Sn–0.25nickel was performed as follows, and the negative electrode active material layer which consists of an Sn–Ni alloy was formed.

[0057]The electrocrystallization conditions at the time of plating prepared 45 g/L of tin chloride, 10 g/L of nickel chloride, 200 g/L of potassium pyrophosphate, 20 g/L of glycines, and the pyrophoric acid bath of ammonia solution 5 ml/L, and made PH 8 and 50 \*\* of bath temperature. The negative electrode active material layer made from an alloy thin film of 1 micrometer of thickness was produced by current density  $0.5 \text{ A/dm}^2$  on the above-mentioned conditions.

[0058]Next, the enveloping layer was formed in the negative electrode active material layer surface.

[0059]To 85 weight % of mesophase pitch system carbon fiber (MCF), first, 5 weight % of graphite, 3 weight % of acetylene black, and 7 weight % of PVdF(s) and a NMP solution were added, and it mixed, and applied to the negative electrode active material layer surface obtained previously by a thickness of 50 micrometers, and after desiccation, by pressing, the enveloping layer was formed and the anode was produced.

[0060]The separator which consists of a porosity film made from <production of electrode group> polyethylene was prepared, after laminating the cathode obtained previously and an anode via this separator, it wound spirally and the electrode group was produced so that said anode might be located in an outermost periphery.

[0061]1.0 mol / L dissolution made lithium hexafluorophosphate ( $\text{LiPF}_6$ ) the <adjustment of nonaqueous electrolyte> pan at (the mixed volume ratio 1:2) at the mixed solvent of ethylene carbonate (EC) and methylethyl carbonate (MEC), and nonaqueous electrolyte was adjusted to it.

[0062]The cylindrical shape nonaqueous electrolyte secondary battery shown in drawing 1 which stored the obtained electrode group and said electrolysis solution, respectively, and mentioned them above in the closed-end cylindrical cup made from stainless steel was assembled.

[0063]Mesophase pitch system carbon fiber which did not use an alloy for negative electrode active material, but was heat-treated at 2900 \*\* as an anode for comparative example 1 comparison (a fiber diameter 7 micrometers) Mean fiber length assembled the nonaqueous electrolyte secondary battery like Embodiment 1 except for 25 micrometers and the average spacing d (002) having used the powder of specific surface area [ of  $2.5 \text{ m}^2/\text{g}$  by 0.35 nm and a BET adsorption method.

[0064]As comparative example 2 anode, the nonaqueous electrolyte secondary battery was created like Embodiment 1 except for not having formed an enveloping layer.

[0065]Except for having replaced the alloy used for two to embodiment 10 negative electrode active material layer with the alloy shown in Table 1, the nonaqueous electrolyte secondary battery was created like

Embodiment 1.

[0066]Each nonaqueous electrolyte secondary battery obtained in the <cell evaluation> embodiments 1-10 and the comparative examples 1 and 2 was evaluated as follows.

[0067]After charging each nonaqueous electrolyte secondary battery to 4.2V by the charging current 1A for 2.5 hours, the charge-and-discharge cycle test discharged by 5A to 2.0V was done. From the result, the high-rate-discharge capacity factor and the capacity maintenance rate (ratio of the service capacity of a 300 cycle eye to that of 1 cycle eye) were measured about each nonaqueous electrolyte secondary battery. The result is written together to the following table 1. A high-rate-discharge capacity factor is a ratio at the time of setting high-rate-discharge capacity of the carbonaceous material anode of the comparative example 1 to 1.

[Table 1]

	負極活物質	被覆層	高率放電 容量	容量 維持率	負極活物質 層厚
実施例 1	0.75Sn-0.25Ni	C	2.1	93%	0.1 $\mu\text{m}$
実施例 2	0.8Sn-0.1Ni-0.1Cu	0.6C-0.4Mg	2.5	95%	0.3 $\mu\text{m}$
実施例 3	0.7Sn-0.3Sb	0.85C-0.05Si	1.7	91%	30 $\mu\text{m}$
実施例 4	0.6Cu-0.5Sn	0.7C-0.3Al	1.9	96%	1.0 $\mu\text{m}$
実施例 5	0.3Sn-0.3Sb- 0.2Cu-0.2Al	0.5C-0.4Si-0.1Mg	2.8	90%	0.05 $\mu\text{m}$
比較例 1	C	—	1.0	95%	20 $\mu\text{m}$
比較例 2	0.75Sn-0.25Ni	—	1.9	5%	10 $\mu\text{m}$

It turns out that the capacity maintenance rate of the nonaqueous electrolyte secondary battery of Embodiments 1-10 of this invention at the time of high-rate-discharge capacity and 300 cycles improves by leaps and bounds compared with nonaqueous electric charge \*\*\*\*\* of the comparative example 2, and it excels in a cycle characteristic so that clearly from Table 1.

[0068]

[Effect of the Invention]As explained in full detail above, according to this invention, a nonaqueous electrolyte secondary battery with a good cycle characteristic can be provided by high-rate-discharge capacity.

[Translation done.]

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] The fragmentary sectional view showing the nonaqueous electrolyte secondary battery concerning this invention.

[Drawing 2] The sectional view showing the anode concerning this invention.

[Explanations of letters or numerals]

1 ... Container

3 ... Electrode group

4 ... Cathode

5 ... Separator

6 ... Anode

11 ... Collecting lead for cathodes

13 ... Collecting lead for anodes

21 — Charge collector

22 — Negative electrode active material layer

23 — Enveloping layer

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[Translation done.]

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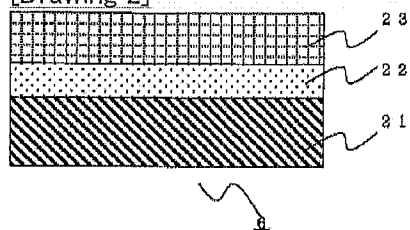
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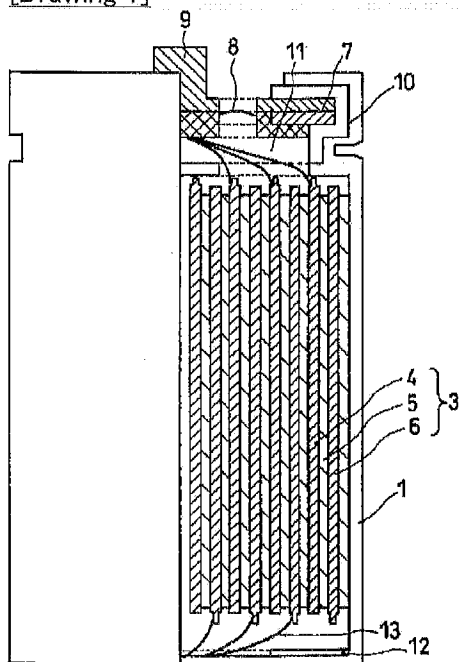
DRAWINGS

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[Drawing 2]



[Drawing 1]



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[Translation done.]



# PATENT ABSTRACTS OF JAPAN

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(72)Inventor : YAMAMOTO HIROSHI

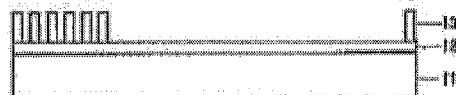
## (54) GRAPHITE THIN FILM, PRODUCTION OF GRAPHITE THIN FILM AND SECONDARY BATTERY AND CAPACITOR USING THE SAME

(57)Abstract:

**PROBLEM TO BE SOLVED:** To prepare a graphite thin film used for an electrode material or the like of a battery and having remarkably large surface area by forming a crystalline structure constituted of a planar thin film part and an erecting thin film part erecting in the vertical direction to the horizontal thin film.

**SOLUTION:** This graphite thin film is constituted of the planar thin film part 12 formed to cover the surface of a base body and the erecting thin film part 13 erecting in the vertical direction to the planar thin film part 12 and having a regularly arranged polygonal net face structure.

The graphite thin film is produced by the following method. (1) Gas plasma is generated by plasma exciting a gaseous compound containing carbon or a mixture of the gaseous compound with hydrogen or a halogen gas as a gaseous starting material. (2) The gas is accelerated up to a flow velocity larger than sonic velocity. (3) The gas plasma is introduced to the surface of a base body to the treated placed in a reduced pressure to form the graphite thin film.



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CLAIMS

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[Claim(s)]

[Claim 1] A graphite thin film comprising a flat-surface thin film part and a standing-up thin film part made to stand up to said flat-surface thin film part by perpendicular direction.

[Claim 2] The graphite thin film according to claim 1, wherein said standing-up thin film part has the polygon mesh plane structure arranged regularly.

[Claim 3] A graphite thin film comprising a flat-surface thin film part which was formed in a base surface, and which was formed in a graphite thin film so that said base surface might be covered, and a standing-up thin film part with polygon mesh plane structure which was made to stand up to said flat-surface thin film part by perpendicular direction, and was arranged regularly.

[Claim 4] A plasma production process of carrying out plasma excitation of the mixed gas with compound gas which contains carbon as material gas or said compound gas, hydrogen, or halogen gas, and generating gaseous plasma, A process of accelerating said gaseous plasma so that it may have the larger rate of flow than acoustic velocity, A manufacturing method of a graphite thin film using a plasma jet process being made to heat by desired temperature, leading said gaseous plasma to a processed base surface put under decompression, and forming a graphite thin film.

[Claim 5] A manufacturing method of a graphite thin film using a plasma jet process forming a graphite thin film characterized by comprising the following.

A plasma production process of carrying out plasma excitation of the mixed gas of  $\text{CH}_4$  and  $\text{H}_2$ , and generating gaseous plasma as material gas.

A process of accelerating said gaseous plasma so that it may have the larger rate of flow than acoustic velocity.

Said gaseous plasma is led to a processed base surface you were made to heat by desired temperature, and it is a flat-surface thin film part.

A standing-up thin film part with polygon mesh plane structure which was made to stand up to said flat-surface thin film part by perpendicular direction, and was arranged regularly.

[Claim 6] A rechargeable battery comprising a graphite thin film characterized by comprising the following.  
The 1st electrode formed in a base surface.

Ion conductor material formed in the upper layer of said 1st electrode.

It comprises the 2nd electrode formed in the upper layer of this ion conductor material, and said 1st electrode is a flat-surface thin film part.

A standing-up thin film part with polygon mesh plane structure which was made to stand up to said flat-surface thin film part by perpendicular direction, and was arranged regularly.

[Claim 7] An electric double layer capacitor which formed many internal electrodes on both sides of a separator which made an electrolysis solution impregnate, comprising:

Said internal electrode is a flat-surface thin film part.

A standing-up thin film part with polygon mesh plane structure which was made to stand up to said flat-surface thin film part by perpendicular direction, and was arranged regularly.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the rechargeable battery and capacitor which used the manufacturing method of a graphite thin film and a graphite thin film, and this, and relates to the graphite thin film which has a new crystal structure especially.

[0002]

[Description of the Prior Art]As a chargeable and dischargeable cell (rechargeable battery), a lead storage battery is the most popular now, in addition a lithium cell, a nickel cell, a manganese cell, etc. are raised especially. A cell is equipment which transforms electrical energy into chemical energy and accumulates it, and comprises combination of positive active material / electrolyte / active material, and an anode. And a reducing agent is used for an oxidizer and negative electrode active material by this cathode and anode at a electron conductive material and an electrolyte at ion-conductive material and positive active material.

[0003]However, although all use a chemical reaction, suitable capacity and weight must have been escaped according to the energy which it is going to conserve, and when considering use to an electromobile or a solar car, the demand to a miniaturization becomes very high.

[0004]For example, as conventionally shown in drawing 16, the positive pole collector 102 is attached to an inner base, The cathode 103 is stuck to the positive electrode can 101 in which the insulating packing 108 was laid by pressure, While laying the separator 107 of fine porosity polypropylene furthermore and making an electrolysis solution impregnate, what the negative pole collector 105 is besides attached to the inner surface of the negative electrode can 104, and sticks the anode 106 by pressure -- the insulating packing 108 -- passing -- the formed coin type lithium battery is proposed by closing (JP,H6-325753,A). Although graphite is used as an anode, a degree of graphitization needs to use the high thing which has high surface area.

[0005]The example using fibrous graphite as a positive electrode material is also proposed (carbon TANSO1991 (No.150)p.319-327). However, the graphite fiber had to be fabricated as a negative electrode plate, and it could not still say that a touch area with an electrolysis solution was large enough, but there was a problem that the portion which can be used effectively was small and especially specific surface area was small.

[0006]Sufficient energy was not able to be acquired although the trial which is going to store the same energy in the conventional laminate type ceramic capacitor on the other hand was also made.

[0007]In order to aim at increase of stored energy, it is an element also with big increase of the touch area of electrode material and ion-conductive material other than improvement of the electrolyte and electrode material which consist of ion-conductive material.

[0008]

[Problem to be solved by the invention]Thus, although the demand to increase of the stored energy of a rechargeable battery is increasing, it cannot obtain sufficient stored energy.

[0009]Then, as an electrode material, a conductive high material with large surface area was called for.

[0010]This invention was made in view of said actual condition, its surface area used for the electrode material of such a cell, etc. is very large, and an object of this invention is to provide the graphite thin film of a completely new structure.

[0011]This invention and an energy density are high by leaps and bounds, and it aims at providing a compact cell.

[0012]

[Means for solving problem]There is the 1st feature of this invention in having constituted from a flat-surface thin film part and a standing-up thin film part made to stand up to said flat-surface thin film part by perpendicular direction.

[0013]Desirably, said standing-up thin film part has the polygon mesh plane structure arranged regularly.

[0014]In a graphite thin film in which the 2nd feature of this invention was formed in a base surface, You are made to stand up to a flat-surface thin film part formed so that said base surface might be covered, and said flat-surface thin film part by perpendicular direction, It is characterized by it being in having comprised a

standing-up thin film part with polygon mesh plane structure arranged regularly that said base substance is molybdenum or a single crystal silicon substrate desirably.

[0015]A plasma production process of the 3rd feature of this invention carrying out plasma excitation of the mixed gas with compound gas which contains carbon as material gas or said compound gas, hydrogen, or halogen gas, and generating gaseous plasma, It is made to heat said gaseous plasma by a process accelerated so that it may become the larger rate of flow than acoustic velocity, and desired temperature, said gaseous plasma is led to a processed base surface put under decompression, and it is in having formed a graphite thin film using a plasma jet process.

[0016]The plasma production process of the 4th feature of this invention carrying out plasma excitation of the mixed gas of  $\text{CH}_4$  and  $\text{H}_2$  as material gas, and generating gaseous plasma, The process of accelerating said gaseous plasma so that it may become the larger rate of flow than acoustic velocity, Lead said gaseous plasma to the processed base surface you were made to heat by desired temperature, and A flat-surface thin film part, It is made to stand up to said flat-surface thin film part by the perpendicular direction, and is in having formed the graphite thin film which consists of a standing-up thin film part with the hex-steel plane structure arranged regularly using the plasma jet process.

[0017]The ion conductor material in which the 5th feature of this invention was formed in the upper layer of the 1st electrode formed in the base surface, and said 1st electrode, Comprise the 2nd electrode formed in the upper layer of this ion conductor material, and said 1st electrode A flat-surface thin film part, It is made to stand up to said flat-surface thin film part by the perpendicular direction, and is in the lithium secondary battery characterized by making it formed with the graphite thin film which consists of a standing-up thin film part with the polygon mesh plane structure arranged regularly.

[0018]In the electric double layer capacitor with which the 6th feature of this invention formed many internal electrodes on both sides of the separator which made the electrolysis solution impregnate, It constituted from a graphite thin film which consists of a standing-up thin film part with the polygon mesh plane structure which was made to stand up this internal electrode to a flat-surface thin film part and said flat-surface thin film part by the perpendicular direction, and was arranged regularly. By the way, where it plasma-ized gas, and was activated with the induction plasma process or DC plasma jet process and reactivity is improved, By turning this plasma-ized gas to a processed base surface, and making it inject at high speed, The technology of performing surface treatments, such as thin film forming, etching, or surface treatment, is publicly known, and is already widely used for surface treatment processing of formation of semiconductor membrane, etching or oxidation, nitriding, etc., etc.

[0019]This invention persons discovered the graphite thin film of the structure where surface area is dramatically large and membrane characteristics are completely very good and new, as a result of repeating various experiments and forming various thin films using a plasma jet process.

[0020]According to the 1st of this invention, and 2, it can obtain with very stably and sufficient reproducibility, and becomes what has very large surface area.

[0021]According to the 3rd of this invention, membraneous quality can form a good and reliable graphite thin film in a processed base surface by spraying a plasma jet.

[0022]According to the 4th of this invention, the graphite thin film which consists of a flat-surface thin film part and a standing-up thin film part with the polygon mesh plane structure which was made to stand up to said flat-surface thin film part by the perpendicular direction, and was arranged regularly can be formed in a processed base surface by spraying a plasma jet.

[0023]Since it constitutes from a graphite thin film which consists of a standing-up thin film part with the polygon mesh plane structure which was made to stand up the 1st electrode to a flat-surface thin film part and said flat-surface thin film part by the perpendicular direction, and was arranged regularly according to the 5th of this invention, A very large touch area with the ion conductor material besides formed in the layer can be taken, and it becomes possible to obtain an efficient rechargeable battery.

[0024]Since it constitutes from a graphite thin film which consists of a standing-up thin film part with the polygon mesh plane structure which was made to stand up an internal electrode to a flat-surface thin film part and said flat-surface thin film part by the perpendicular direction, and was arranged regularly according to the 6th of this invention, A very large touch area with an electrolysis solution can be taken, and it becomes possible to obtain a mass capacitor.

[0025]It may be made to perform supply of material gas with inactive gas, such as argon, here as carrier gas.

[0026]

[Mode for carrying out the invention]Hereafter, it explains in detail, referring to Drawings for the embodiment of this invention.

[0027]The graphite thin film of this invention embodiment shows drawing 1 a section explanatory view, and. As the photograph of the crystal structure photoed with the electron microscope is shown in drawing 2 thru/or drawing 6, It is characterized by being what consists of the flat-surface thin film part 12 formed in the surface

of the  $n^+$  type single crystal silicon substrate 11, and the standing-up thin film part 13 with the polygon mesh plane structure which was made to stand up to this flat-surface thin film part 12 by the perpendicular direction, and was arranged regularly.

[0028]The 30k times as many enlargements in which, as for drawing 2, 10k times and drawing 3 took 30k times as many flat-surface enlargements and drawing 4 from the direction of 40 angles of inclination, the 30k times as many enlargements which took drawing 5 from the perpendicular direction, and drawing 6 are the 50k times as many enlargements taken from the perpendicular direction here.

[0029]Drawing 7 is a figure showing a Raman spectrum of this graphite thin film.

[0030]Next, equipment which forms this graphite thin film is explained.

[0031]As this equipment is what used a plasma jet process and it is shown in drawing 8, Impress the 13.56-MHz high frequency current to the induction coil 1 from RF generator 2, and plasma excitation of the material gas which flows through inside of Laval nozzle 3 made from quartz is carried out, A graphite thin film is formed by generating gaseous plasma and leading this to the surface of the  $n^+$  type single crystal silicon substrate 11 installed in the vacuum chamber 4 at a supersonic speed. A substrate as a processed base substance is constituted so that it can maintain to a desired temperature with the heater 6 formed in a substrate supporting stand, and while the thermo couple 8 detects temperature, it is controlling service voltage to a heater of the power supply 7 for heaters by the temperature controller 9 here.

[0032]Laval nozzle 3 which is a supersonic nozzle comprises a Laval nozzle (it is also called a divergent nozzle) under the conditions mentioned later so that the material gas which passes through the inside of a nozzle may carry out adiabatic expansion and may be injected at the larger rate of flow  $u$  than sonic  $a$  from the nozzle exit 3e.

[0033]The gas inlet 3a (20mmphi) which supplies the material gas which should be injected on the surface of the wire rod which Laval nozzle 3 is inside Sai's nozzle, and is a processed base substance, The gas introducing pipe 3b constituted so that a cross-section area might become small gradually with gas advance, You are made for a cross-section area to be gradually expanded with a predetermined angle of divergence from the throat part 3c which makes the cross-section area  $A_1$  (diameter  $d_1$ :10mmphi) minimum with the whole nozzle, and this throat part, It comprises the gas injection pipe 3d with which plasma flow  $P$  is injected from the gas injection mouth 3e of the maximum sectional area  $A_2$  (diameter  $d_2$ :22mmphi). And in the outside of the throat part 3c, it is the induction coil 1 (coil diameter: 16 mm) as a plasma production means. The number of coiling: Five is wound, if the high frequency current energizes to this induction coil 1, an derivation electromagnetic field will be formed in the throat part 3c, and plasma excitation of the gas which passes the throat part 3c is carried out. Thus, it is plasma-ized good by the throat part 3c with the minimum cross-section area  $A_1$ . And towards the substrate, it is constituted so that plasma flow  $P$  may be injected from the injection tip 3e of Laval nozzle 3.

[0034]Next, the formation method of the graphite thin film using this equipment is explained. First, while the  $n^+$  type single crystal silicon substrate 11 is installed in a substrate supporting stand as the processed base substance 5 and the temperature controller 9 performs temperature control, it controls so that substrate temperature maintains 800 \*\*.

[0035]And evacuation of the inside of the vacuum chamber 4 is carried out using a vacuum pump (not shown), a pressure is set to 0.1Torr, and the mixed gas of  $CH_4$ :50 cc/min. and  $H_2$ :500 cc/min. is supplied to Laval nozzle 3 from the gas inlet 3a as material gas.

[0036]And in the throat part 3c, if RF generator 2 is set as an ON state and the high frequency current (1 kW, 13.56 MHz) flows into the induction coil 1, an derivation electromagnetic field occurs in a pipe, heating excitation will be carried out by the energy of this place, and high-density gas will be plasma-ized.

[0037]And expansion acceleration is carried out for the breadth of a nozzle with the blow-of-gas pipe 3d of the downstream, and the plasma-ized high density gas is set to supersonic plasma flow  $P$  from the gas injection mouth 3e, and is injected. Draw this plasma flow  $P$  on the processed base substance 5 at a supersonic speed, and by membrane formation processing of 1 hour, section structure is shown in drawing 1, and. As the electron microscope photograph taken for various angles and magnifications is shown in drawing 2 thru/or drawing 6, the graphite thin film G which consists of the flat-surface thin film part 12 and the standing-up thin film part 13 with the polygon mesh plane structure which was made to stand up to this flat-surface thin film part 12 by the perpendicular direction, and was arranged regularly is formed.

[0038]By the way, the ratios  $P_1/P_0$  of the stagnation pressure  $P_0$  of the material gas 6 and the pressure  $P_1$  of the lower stream of the injection tip 4a which were introduced [ according to the theory of gas dynamics ], for example in the case of a two-atom gas, When the ratios (Suehiro ratio)  $A_2/A_1$  of the cross-section area  $A_1$  of about 0.52 or less and the throat part 3c to the cross-section area  $A_2$  of the injection tip 3e exceed 1, adiabatic expansion of the gas is carried out and the injection rate of flow turns into the larger rate of flow  $u$  than the supersonic speed  $a$ , i.e., acoustic velocity.

[0039]Since exfoliation of a boundary layer will occur on a wall surface if not much large, the angle of divergence before and behind the throat part 3c needs to make it a suitable about size, for example, 15 degrees.

[0040]However, since it is designed mention above so that the material gas which passes an inside may carry out adiabatic expansion, Laval nozzle 1 is quenched in this adiabatic expansion process, and by the time it reaches a processed base surface, it will become a suitable temperature of the grade which does not produce degradation of a processed base substance. Since the temperature at this time is decided by the above-mentioned Suehiro ratios  $A_2/A_1$  (this example 0.4), it can acquire arbitrary temperature according to the design condition of the nozzle 1.

[0041]Since plasma flow has a supersonic speed, time until it reaches a processed base substance is very short, and the state where it was excited by heating and plasma-ization by the time it reached the processed base substance does not return to the original state. Thus, temperature can be lowered to optimal temperature, with what is called an excitation state maintained. Therefore, membranous quality can be raised. Since injection is completed for a short time, membrane formation speed will increase and working efficiency will also improve.

[0042]The phenomenon explained above is explained as follows by the theory of one-dimensional-flow physical strength study.

[0043]That is, the fluid temperature in the adiabatic flow of perfect gas and the relation of the rate of flow are expressed by the following formula.

[0044]

$$T_0 = T + (1/2) - \{(\gamma - 1) / (\gamma - R)\} - (u)^2 \quad (1)$$

$$\text{Or } T_0/T = 1 + \{(\gamma - 1) / 2\} \text{ and } (M)^2 \quad (2)$$

It is the total temperature (almost equal to the temperature of the throat part 3 which is a heating unit) of a  $T_0$ :flow here.

T: Static temperature of a flow (what is called temperature)

$\gamma$ : It is a rate-of-flow M:Mach number into which gas ratio-of-specific-heat R:Gas-constant u: Flows.

[0045]The above-mentioned (2) formula rewrites the above-mentioned (1) formula using a Mach number ( $u/a$ , a: acoustic velocity). Mach number M is uniquely determined as a function of Suehiro ratio  $A_2/A_1$ .

[0046]since the value of total temperature  $T_0$  is kept constant in an adiabatic expansion process from the above-mentioned (1) formula — the increase in the rate of flow  $u$  — it both turns out that the fall of the static temperature  $T$  takes place. That is, a rapid temperature fall takes place, so that the speed of a flow is large.

[0047]A value of thermal-ratio  $T_0/T$  increases from the above-mentioned (2) formula in proportion to a square of Mach number M. For example, in the case of a two-atom gas ( $\gamma = 1.4$ ), it is set to thermal-ratio  $T_0/T = 6$  at the time of Mach number  $M = 5$ . That is, by carrying out the adiabatic expansion acceleration of the reactant plasma heated by elevated temperature to a high Mach number using Laval nozzle 1 shows that plasma temperature  $T$  can be lowered to a temperature suitable for the single crystal silicon substrate 11 which is a processed base substance. Since plasma particles are accelerated at very high speed at this time. Time until it reaches (for example, it is set to  $u = 5123$  (m/s) in the case of  $T = 1500$ (K),  $\gamma = 1.4$ ,  $R = 500$  (J/kgK), and  $M = 5$ ) and a processed base substance is dramatically short, and the plasma can reach a processed base substance at low temperature, maintaining an initial activity state mostly.

[0048]Although said embodiment explained an example which used a single crystal silicon substrate as a substrate, without being limited to single crystal silicon, it may be made to use other materials and can form also on metallic bases, such as Mo, nickel, and Fe, or an insulating substrate.

[0049]An electron microscope photograph at the time of forming a graphite thin film on the same conditions as said embodiment on Mo board is shown in drawing 9 thru/or drawing 11. 30k times as many enlargements in which drawing 9 took 30k times as many flat-surface enlargements and drawing 10 from the direction of 40 angles of inclination, and drawing 11 are the 50k times as many enlargements taken from the direction of 40 angles of inclination here. It turns out that it is made to stand up to this with a flat-surface thin film part similarly on Mo board so that these photographs may show by perpendicular direction, and a graphite thin film which consists of a standing-up thin film part with polygon mesh plane structure arranged regularly is formed.

[0050]although various conditions can be changed here, on the occasion of plasma excitation, supplied power is enlarged with about 800–1000w — required — certain \*\* It is desirable to consider it as 600–800 \*\* also about temperature. As for the pressure of a vacuum chamber, it is still more desirable to use 0.1 or less.

[0051]In an embodiment, although plasma excitation of the gas is carried out with the induction coil, on the occasion of plasma excitation, ECR plasma, the Helicon plasma, etc. may use other plasma excitation means.

[0052]Thus, when the lithium secondary battery of button mold structure as shown in drawing 12 was formed using the obtained graphite thin film as an anode, the life of 1500 or more cycles was able to be attained with the capacity and 100% depth of discharge of 3000 or more mAh/kg. With the large improvement in the electrode area by having used the anode 14 which has a detailed graphite structure like sponge, this is considered to be

for a high degree of graphitization. It is the same as that of the lithium secondary battery of the conventional example which the graphite thin film of this invention was used for the anode here, and also was shown in drawing 16, and it constitutes so that the separator 107 of fine porosity polypropylene may be made to impregnate an electrolysis solution and this may be inserted with the cathode 103. Identical codes were given to the same element as the component of the lithium secondary battery shown by drawing 16, and explanation was omitted.

[0053]The graphite film of this invention can be directly formed on a metallic foil, becomes insoluble [ a binding agent ], and can improve a storage capacity. Manufacture can form very easily [ it is easy and ] only by improvement in \*\*\*\* capacity laminating an anode with a graphite film, and a separator cathode simply.

[0054]Incidentally, it was formed by mixing a binding agent with natural graphite and a cupric oxide, applying to a metallic foil, a metallic mesh, a three-dimensional porous body, etc., pressing after desiccation and heat treatment, carrying out reduced pressure drying further, and conventionally, performing water removal, and there was a problem that a manufacturing process was very complicated. Since binding capacity was not demonstrated but omission of black lead etc. occurred if a binding material is not larger than 90:1, there was a problem that a binding material was indispensable, there were few amounts of volume integral black lead of a binding material, and storage capacitance could not be enlarged enough. On the other hand, according to the lithium secondary battery of this invention, a problem which was mentioned above is solved and can obtain the rechargeable battery whose storage capacitance it is small and is large. In addition to this, this invention is applicable also to the lithium secondary battery of cylindrical structure.

[0055]As shown in drawing 13, also when this graphite thin film is used as the internal electrode 24 of an electric double layer capacitor, it becomes possible to attain large scale-ization. 25 is a separator made from fine porosity polypropylene here, and 26 is an electrode.

[0056]Here, the internal electrode 24 used what formed 1 hour of one side at a time the graphite thin film of 1-micrometer-thick this invention in the surface of a copper plate (20 mm in diameter, and 0.1 mm in thickness) on  $H_2$  flow 500sccm,  $CH_4$  flow 50sccm, high frequency output 1kw, and conditions with a cooking temperature of 800 \*\*. 100 layers of electrode plates which sandwiched the separator made from fine porosity polypropylene in between by using the 0.5M propylene carbonate solution of  $PBF_4$  as an electrolysis solution are laminated, and it is considered as an anode and a cathode by turns ( $C_2H_5$ ).

[0057]Thus, when charge voltages were charged in 3V at the formed electric double layer capacitor and capacity density was measured, 30 – 40 Wh/L was obtained. Although the charging and discharging cycle was repeated 100,000 times or more, was carried out and the fall of capacity density was measured, there was only 5% or less of capacity density fall, and it was very long lasting.

[0058]In addition, the graphite thin film of this invention can provide a vast touch area by using as catalyst support. By forming in the surface and the rear face of the base substance 31 the graphite thin film G which consists of the flat-surface thin film part 32 and the standing-up thin film part 33, as shown in drawing 14, catalyst support with very large surface area can be constituted. For example, when the intercalation of Li, K, H-Hg, K- $FeCl_3$ ,  $Br_2$ ,  $H_2SO_4$ , and the Fe was carried out to this catalyst support and it was used for it as a catalyst of an organic reaction, compared with the former, the reaction was able to be gone on at the speed of 10 times or more.

[0059]A graphite thin film of this invention is effective also as a hydrogen absorption material. As shown in drawing 15, a hydrogen absorption material with very large surface area can be constituted by forming the graphite thin film G which consists of the flat-surface thin film part 42 and the standing-up thin film part 3 in the surface of the particles 41 which consist of graphite of desired particle diameter. using a graphite thin film of this invention, although a graphite thin film is forming an intercalation compound with potassium and hydrogen absorption and discharge are repeated -- RU -- hydrogen absorption and a releasing speed became 10 or more times by things compared with the former. A cycle life was able to be raised to 10000 cycles.

[0060]When a substrate was used as molybdenum and silicon further again when forming a graphite thin film using equipment shown by drawing 8,  $CH_4$  gas mass flow and concentration were changed, respectively, and a graphite film was judged with a microphotograph. It is a time of methane concentration being more than the specified quantity, as shown in the following table that a good graphite thin film of this invention is formed as a result, and it turns out that a direction at the time of using a molybdenum substrate can form a good high specific surface area graphite thin film compared with a silicon substrate.

[0061]

No.	基板	メタン濃度	流量	高比表面積グラファイト膜
1	Mo	5 %	525 sccm	○
2	Mo	2	510	○
3	Mo	2	1020	×
4	Mo	1	1010	×
5	Si	10	550	○
6	Si	5	525	○(成長不足)
7	Si	2	510	×
8	Si	1	2020	×
9	Si	1	1010	×

1kw substrate temperature made the high frequency output 800 \*\* here.

[0062]

[Effect of the Invention]According to this invention, as explained above, surface area is very large, a graphite thin film with the high degree of black lead can be obtained, and this is very effective as various element materials, such as an electrode material of a lithium secondary battery. According to the method of this invention, a graphite thin film can be obtained with sufficient reproducibility very easily.

[Translation done.]



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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]The typical sectional view showing the graphite thin film of this invention embodiment

[Drawing 2]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 3]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 4]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 5]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 6]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 7]The figure showing the Raman spectrum of the graphite thin film

[Drawing 8]The figure showing a film deposition system in order to form the graphite thin film

[Drawing 9]The electron microscope photograph in which the crystal structure of the graphite thin film of other embodiments of this invention is shown

[Drawing 10]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 11]The electron microscope photograph in which the crystal structure of the graphite thin film is shown

[Drawing 12]The figure showing the lithium secondary battery using the graphite thin film of this invention embodiment

[Drawing 13]The figure showing the electric multiplex layer capacitor using the graphite thin film of this invention embodiment

[Drawing 14]The figure showing the catalyst support using the graphite thin film of this invention embodiment

[Drawing 15]The figure showing the hydrogen absorption material using the graphite thin film of this invention embodiment

[Drawing 16]The figure showing the usual lithium secondary battery

[Explanations of letters or numerals]

1 Induction coil

2 RF generator

3 Laval nozzle

3b Gas introducing pipe

3a Gas inlet

3c Throat part (throat)

3d gas injection pipe

3e Gas injection mouth

4 Vacuum chamber

5 Processed base substance

6 Heater

7 The power supply for heaters

8 Thermo couple

9 Temperature controller

P plasma flow

11 Single crystal silicon substrate

12 Flat-surface thin film part

13 Standing-up thin film part

14 Anode

24 Internal electrode  
25 Separator  
26 Electrode  
31 Base substance  
32 Flat-surface thin film part  
33 Standing-up thin film part  
41 Particles  
42 Flat-surface thin film part  
43 Standing-up thin film part  
G Graphite thin film  
101 Positive electrode can  
102 Positive pole collector  
103 Cathode  
104 Negative electrode can  
105 Negative pole collector  
106 Anode  
107 Separator  
108 Insulating packing

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[Translation done.]

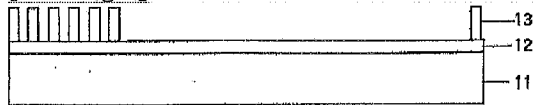
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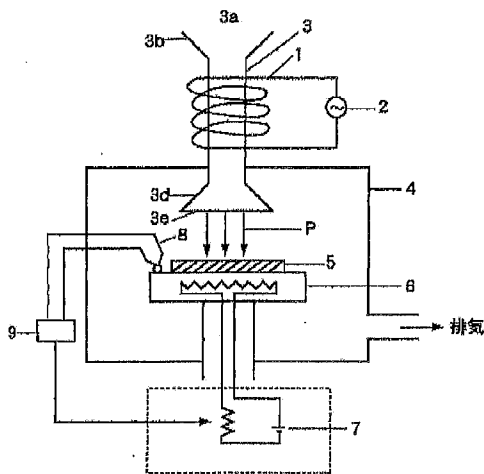
## DRAWINGS

[Drawing 1]



[Drawing 8]

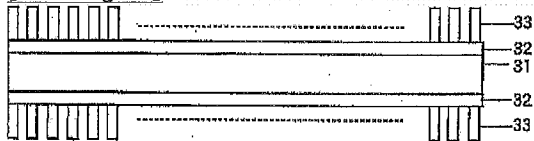
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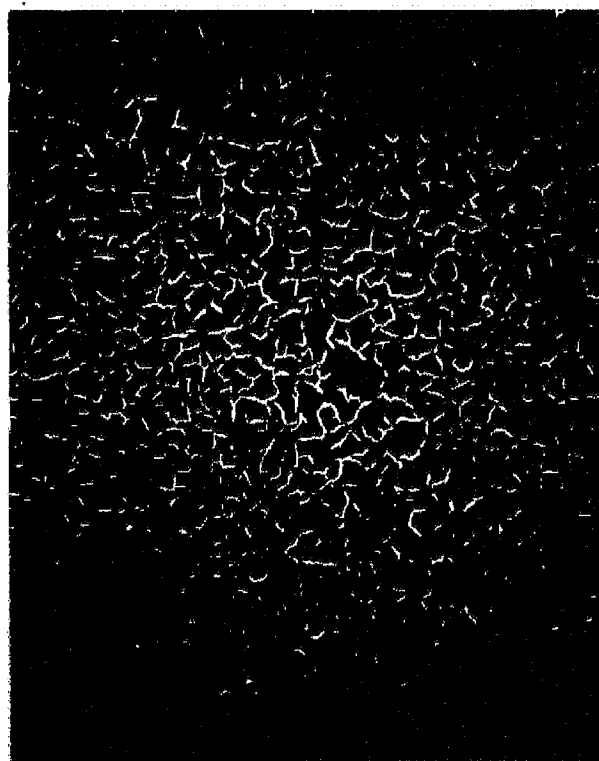
[Drawing 13]



[Drawing 14]



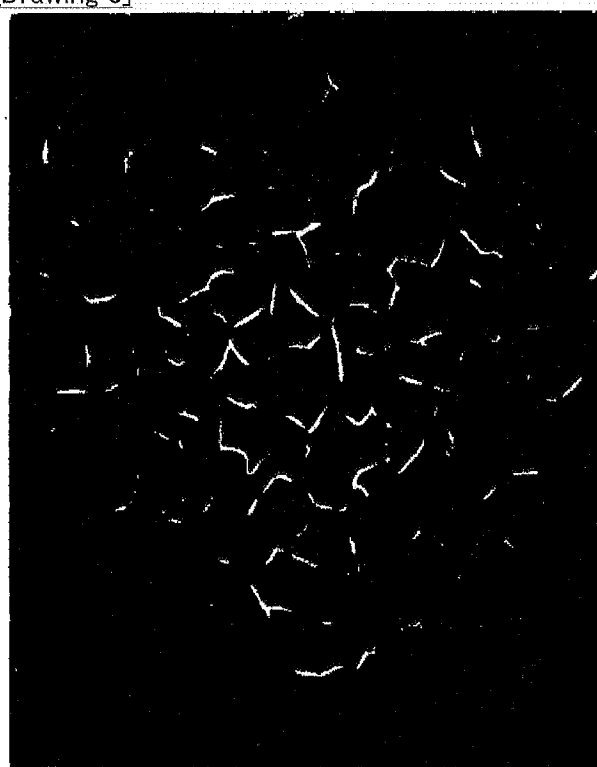
[Drawing 2]



N+S i 基板表面

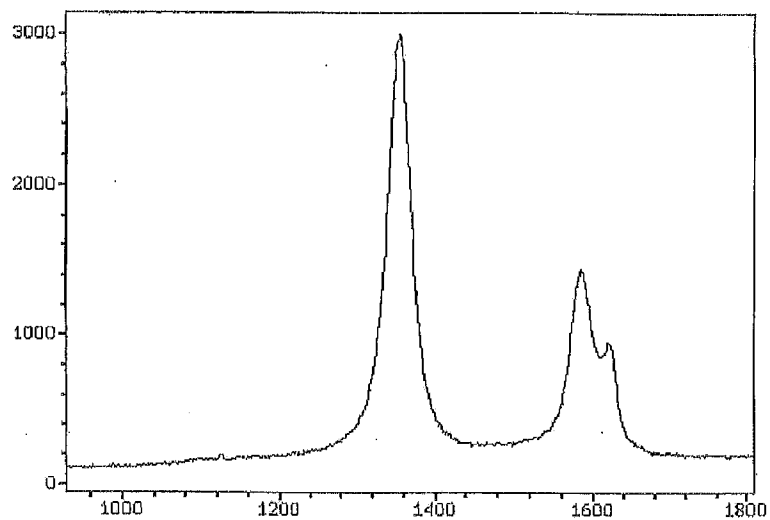
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[Drawing 3]

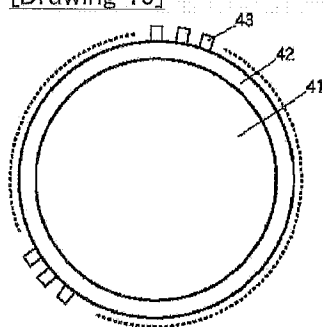


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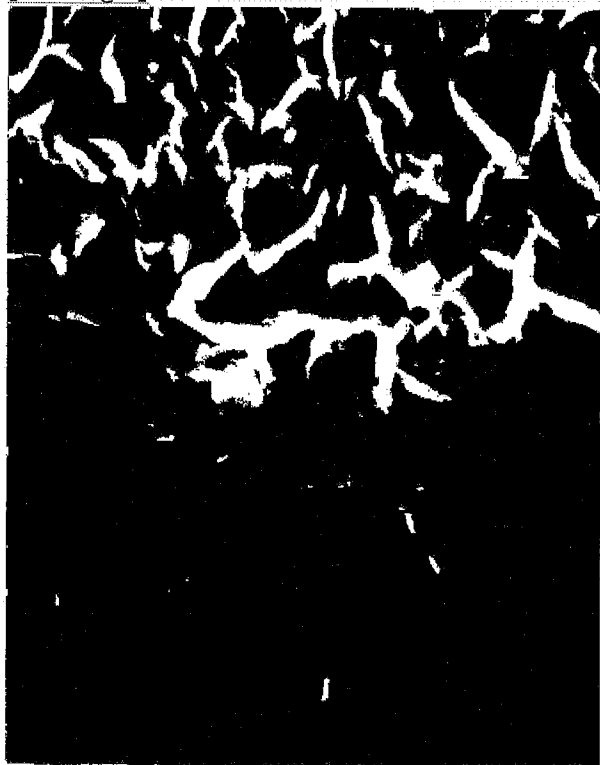
[Drawing 7]



[Drawing 15]



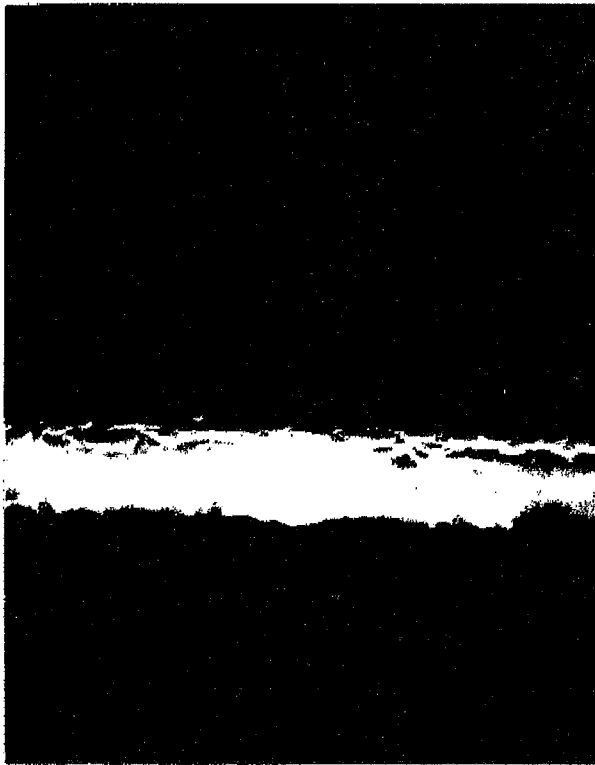
[Drawing 4]



N+Si 基板 傾斜 40°

×30k

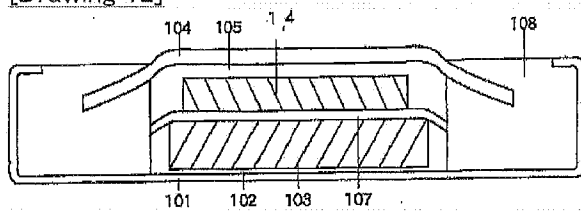
[Drawing 5]



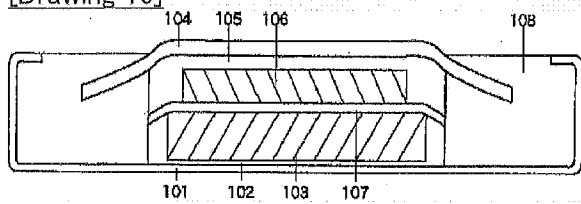
垂直

×30k

[Drawing 12]



[Drawing 16]



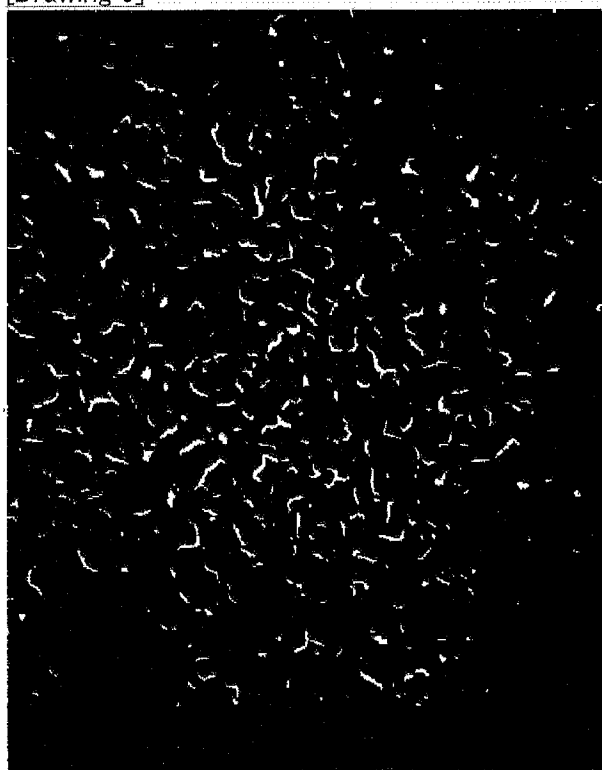
[Drawing 6]



垂直

×50k

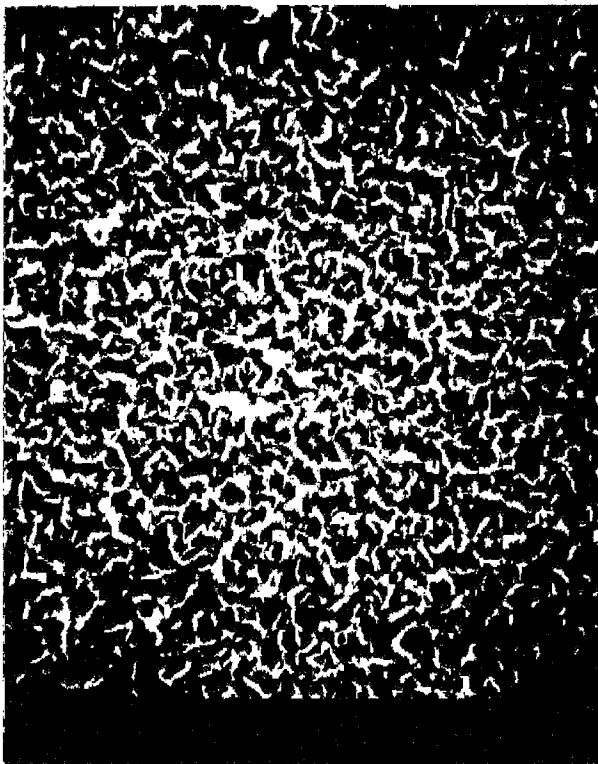
[Drawing 9]



M<sub>0</sub> 基板表面

×30k

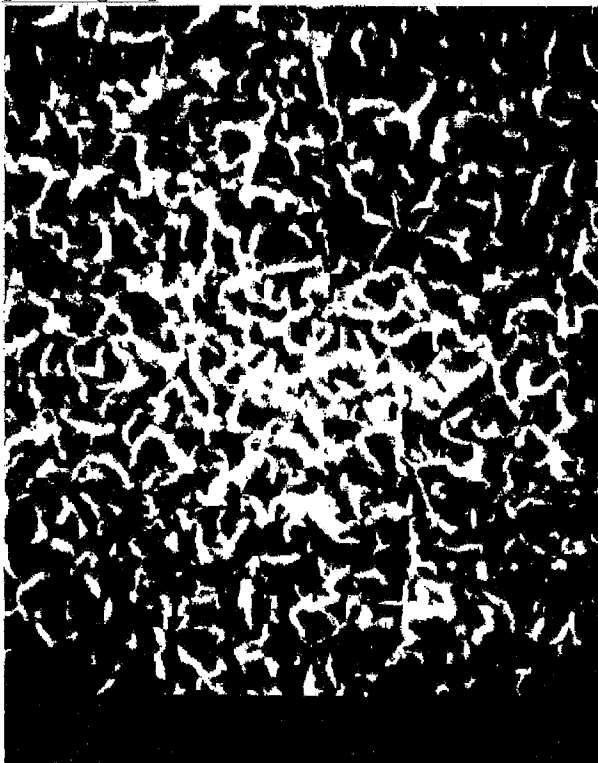
[Drawing 10]



傾斜 4 0°

×30k

[Drawing 11]



傾斜 4 0°

×50k

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[Translation done.]



# PATENT ABSTRACTS OF JAPAN

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(21)Application number : 06-116299

(71)Applicant : MITSUBISHI CABLE IND LTD

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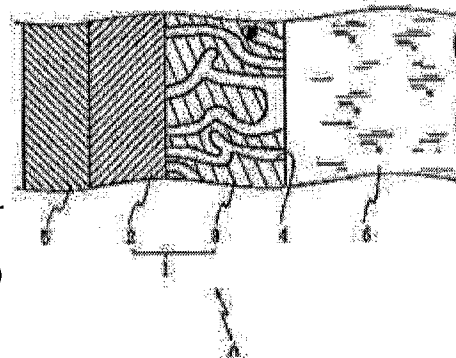
(72)Inventor : SOEJIMA HIROSHI  
TAKADA YOSHINORI

## (54) NEGATIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY, AND LITHIUM SECONDARY BATTERY USING THE SAME

(57)Abstract:

PURPOSE: To provide a negative electrode for lithium secondary battery which has a large charge/discharge capacity and a high electromotive force, and is minimized in the deterioration by repeat of charge/discharge, and a lithium secondary battery using this negative electrode.

CONSTITUTION: This negative electrode A for lithium secondary battery has a laminated body having a porous layer 3 consisting of Li alloy formed on the surface of a carbon layer 2. The Li alloy used in the porous layer 3 has a characteristic that the speed of absorption and release of Li is slow, compared with the carbon used in the carbon layer 2, and Li-Si alloy or Li-Zn alloy is particularly preferred. The composition ratio of each alloy is most preferably about Li:Si=1:(3.3-4.4) in the Li-Si alloy and about Li:Zn=1:(1-1.5) in the Li-Zn alloy.



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**CLAIMS**

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[Claim(s)]

[Claim 1] An anode for lithium secondary batteries having a layered product which comes to form a porous layer which consists of a Li alloy on a carbon layer as an active material layer.

[Claim 2] The anode for lithium secondary batteries according to claim 1 whose Li alloy is Li-Si alloy or a Li-Zn alloy.

[Claim 3] The anode for lithium secondary batteries according to claim 2 whose composition ratio of Li-Zn alloy composition ratio (ratio of the number of constituent elements) of Li-Si alloy is Li:Si=1: (3.3-4.4), and is Li:Zn=1: (1-1.5).

[Claim 4] A lithium secondary battery provided with the anode for lithium secondary batteries according to any one of claims 1 to 3.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the anode for lithium secondary batteries excellent in the cycle life concerning charge and discharge, and the lithium secondary battery which uses the anode while having higher electromotive force and large service capacity in detail about a lithium secondary battery.

[0002]

[Description of the Prior Art] Li is the raw material outstanding as an active material for the anodes of a rechargeable battery from the field of charge-and-discharge capacity and electromotive force. However, lithium has the character to be easy to grow up as a needlelike crystal (dendrite) in the case of the deposit to up to the anode at the time of charge, and this dendrite generates various problems. When the method of growth of the above-mentioned Li dendrite is what repeats growth and lack, since supply of an electric charge is severed, this missing Li is not related to charge and discharge in many cases. Therefore, Li is exhausted more than needed and a charge-discharge cycle characteristic deteriorates. When the method of growth of Li dendrite is what continues growth without being missing, this needlelike crystal will contact a cathode finally and will cause a short circuit trouble. In order to solve these troubles conventionally, using carbon or Li alloys (Li-Si, Li-Zn, etc.) as a material of an anode is made. However, a carbon anode has the problem that electromotive force is low, although comparatively big service capacity is obtained. On the other hand, although the anode by Li alloys, such as Li-Si and Li-Zn, showed electrode potential high like it is equal to Li and generated higher electromotive force, since the speed of absorption and discharge of Li was low, charge-and-discharge capacity was small, and there was a problem of not being practical.

[0003]

[Problem to be solved by the invention] The purpose of this invention is to provide the anode for lithium secondary batteries with little degradation especially by repetition of charge and discharge, having electromotive force with it. [ large charge-and-discharge capacity and ] [ high ] Other purposes of this invention are to provide the lithium secondary battery which are large scale and higher electromotive force, and was excellent in the cycle life of charge and discharge using the above-mentioned anode for lithium secondary batteries.

[0004]

[Means for solving problem] The anode for lithium secondary batteries of this invention has the following features.

- (1) The anode for lithium secondary batteries having a layered product which comes to form the porous layer which consists of a Li alloy on a carbon layer as an active material layer.
- (2) The anode for lithium secondary batteries given in (1) given Li alloy is Li-Si alloy or a Li-Zn alloy.
- (3) The anode for lithium secondary batteries given in (2) the composition ratio (the number of constituent element is the same as that of a ratio and the following) of Li-Si alloy is Li:Si=1: (3.3-4.4), and the given composition ratio of Li-Zn alloy is Li:Zn=1: (1-1.5). The lithium secondary battery of this invention equips either of above-mentioned (1) - (3) with the anode for lithium secondary batteries of a description.

[0005] A figure is used for below and composition for the anode for lithium secondary batteries of this invention to turn into an anode which has each feature of carbon and Li alloy is explained to it. Drawing 1 is a figure in which expanding selectively an example of the anode for lithium secondary batteries of this invention (the following, "anode") as some lithium secondary batteries, and showing it typically. As shown in the figure, the composition of the anode A of this invention has a layered product which comes to form the porous layer 3 which consists of a Li alloy on the carbon layer 2 as the active material layer 1. In the figure, a conductor layer and 6 are electrolysis solutions the hole which exist in the porous layer 3 which consists of a Li alloy 4, and 5, and the surface of the carbon layer 2 is exposed to the electrolysis solution 6 by this hole 4. The lithium secondary battery of this invention is a rechargeable battery which uses the anode for lithium secondary batteries of this invention, and is formed in this anode as various modes combining predetermined essential elements, such as a cathode, a separator, an electrolyte, and a case.

[0006]

[Function] By considering an anode as the above composition, carbon and Li alloy are united in the same electrolysis solution, it is electrically connected and exists as one anode, and as moreover shown in drawing 1, when it sees from the electrolysis solution 6 side, the carbon layer 2 will exist in the very back of the hole 4 which the porous layer 3 has. The following three main operations are shown by such composition.

(1) In a charge-and-discharge process, don't carry out electrocrystallization of the Li ion in an electrolysis solution on Li alloy of a porous layer, but it passes the hole in this Li alloy, and carries out electrocrystallization preferentially on a carbon layer. This operation is the feature in respect of [ in this invention ] material selection.

Absorption of Li [ as opposed to / compared with carbon / an electrolyte in Li alloy ] and the speed of discharge are because it has the loose characteristic.

In detail, the polarization resistance of the anodic dissolution and electrocrystallization of Li in the surface of this Li alloy is because it is larger than it in the surface of carbon. Since Li alloy absorbs Li and cannot emit it easily compared with carbon if Li alloy and carbon are used as an active material layer of an anode in one, the electrocrystallization and anodic dissolution of Li in the active material layer of an anode advance preferentially on the carbon surface.

(2) A carbon layer shares big service capacity and the porous layer which consists of a Li alloy shares high electromotive force generating. This operation is what is obtained by the feature of the structural face of this invention. Though the operation that Li deposits preferentially is efficiently employed in the carbon surface which is the feature of the material selection side of the above (1), this is an opposite operation, i.e., the operation that the characteristic of carbon and the characteristic of the above-mentioned Li alloy are compatible. Namely, in order for Li ion to reach on a carbon layer. By the structure where it must pass through the inside of the hole of Li alloy, also in the interface of Li alloy and an electrolysis solution, the electrochemical reaction of Li ion comes to advance reversibly, generates electrode potential, and a carbon layer and Li alloy layer An anode function is shared. That is, although Li deposits preferentially to carbon, the existence value of Li alloy is not lost by this, either and can demonstrate the characteristic by it.

(3) Since the surface area as the whole active material layer becomes large enough, the current density to the surface becomes small. This operation is not referred to as only being obtained with the porosity of an active material layer, and is materialized under the above (1) and an operation of (2). Li is distributed suitably and an intensive deposit is controlled by this.

[0007] As a carbon material used for a carbon layer, a high crystalline thing is preferred, and graphite, natural graphite, etc. are illustrated.

[0008] As a Li alloy which forms a porous layer, as long as the purpose of this invention can be attained, there is no restriction in particular, for example, the following are mentioned. Li-M1-Te system alloy. However, M1 is a kind of metal chosen from Ag, Zn, Ca, aluminum, Mg, etc., or two or more sorts of alloy contents, and the composition ratio (the number of constituent element is the same as that of a ratio and the following) is Li:M1:Te=80-150:1-20:0.001-2. Li-M2-Cd system alloy. However, M2 is a kind of metal chosen from Sn, Bi, Pb, In, etc., or two or more sorts of alloy contents, and the composition ratio is Li:M2:Cd=70-90:10-30:10-30. Li-M3-Si system alloy. However, M3 is a kind of metal chosen from rare earth metals, such as aluminum, Y, Fe, and Er, or two or more sorts of alloy contents, and the composition ratio is Li:M3:Si=5-7:0.5-2:1-2. Li-In-Zn system alloy (composition ratio Li:In:Zn=2-6:0.5-1.5:0.5-1.5). Li-Ag system alloy (composition ratio Li:Ag=80-99:1-20). In addition, Li<sub>6</sub>Hg, Li<sub>4</sub>Ba, Li<sub>2</sub>Ca, Li<sub>5</sub>Pd, Li<sub>5</sub>Pt, Li<sub>23</sub>Sr<sub>6</sub>, etc. are illustrated. Li-Si and Li-Zn are desirable negative pole materials in which high electromotive force is acquired. the composition ratio of Li-Si alloy — a Li:Si=1: (1-10) grade — it is preferably desirable at Li:Si=1: (3-5) and the point of holding high electromotive force Li:Si=1: (3.3-4.4) controlling a deposit of the crystal of metal lithium especially. the composition ratio of Li-Zn alloy — a Li:Zn=1: (0.5-5) grade — desirable — Li:Zn=1: (0.8-3) — Li:Zn=1: (1-1.5) is especially preferred by the same Reason as the case of the above-mentioned Li-Si alloy.

[0009] The purpose of making into porosity the layer which consists of a Li alloy is to expose the surface of a carbon layer to the electrolysis solution 6 in the very back of the hole inside Li alloy as mentioned above. therefore — the porosity in this Description refers to that to which many detailed holes exist irregularly or regularly in material — an electrolysis solution — this hole from one field of material — it permeates inside and let what can be well open for free passage to other fields (contact surface with a carbon layer) be a desirable thing. The porosity in the case of making into porosity the layer which consists of a Li alloy is suitable for the Reason for raising the diffusing power of ion, without using voidage and reducing electromotive force 50 to 60% of preferably especially 30 to 70% preferably about 20 to 80%.

[0010] Although the method in particular of forming a porous layer using the above-mentioned Li alloy is not restricted, various kinds of vacuum deposition is used and a sintering process, an application-of-pressure casting process, and a spraying process are especially mentioned as a desirable method.

[0011] A sintering process is the method of forming foam by carrying out diffused junction of the raw material metal particles with heating. In this method, the particles of Li alloy are first produced by the gust MAIZU



method. The gust MAIZU method is the method of injecting molten metal via a nozzle in a decompressed atmosphere, and making metal particles. A volatile organic solvent is added to the constant rate of the particles of this Li alloy, and mobility is given, it is considered as a paste state thing, and this paste state thing is developed on the conductor layer tape which consists of good conductor metals, such as Cu and aluminum. Subsequently, this is heated at about 120 \*\*, diffused junction of the particles of Li alloy is carried out at the same time it carries out vaporization of the organic solvent, and foam is obtained. Diffused junction of the particles of Li alloy can be carried out also by being stuck by pressure lightly after the vaporization of an organic solvent. As for the diameter of metal particles of a raw material, about 1-50 micrometers is preferred, and especially 5-20 micrometers have the detailed and precise porous voice formed, and is preferred from the point of moreover not spoiling the absorptivity of a viscous high electrolysis solution.

[0012]An application-of-pressure casting process is the method of carrying out application-of-pressure casting of the raw material metal of the liquid phase into porous particles, such as porous glass bead particles and a porous carbon particle. First, a volatile organic solvent is added to the specified quantity of porous particles, mobility is given, and it is considered as a paste state thing. This paste state thing is developed on the same conductor layer tape as the above, and vaporization of the organic solvent is carried out by stoving. Subsequently, application-of-pressure casting of the Li alloy of the liquid phase is carried out between porous particles, after making porosity particles grind by pressing the whole, it cleans ultrasonically in nonpolar solvents, such as hexane, the ground porosity particles are removed, and foam is obtained.

[0013]A spraying process is the method of adjusting spray coating parameters, such as a powder grain size, spraying distance, and a cooling rate, and forming a porous film. Spray coating is a plasma metal spray and forms a film in an argon normal pressure atmosphere or a decompressed atmosphere.

[0014]The conductor layer 5 is a current path called a charge collector depending on the form of a cell. The carbon layer 2 is formed on this conductor layer 5.

As a material of the conductor layer 5, the metal of a good conductor is preferred and Au, Ag, nickel, etc. besides Cu and aluminum are illustrated.

[0015]The outstanding lithium secondary battery can be formed by using the anode for lithium secondary batteries of this invention. It is not limited especially as a positive electrode material which constitutes the cathode of this lithium secondary battery. Usually, the positive electrode material used for the cathode of a lithium secondary battery can be used. For example,  $V_2O_5$ ,  $MnO_2$ ,  $LiMn_2O_4$ ,  $LiCoO_2$ ,  $LiNi_{0.5}Co_{0.5}O_2$ ,  $LiNiO_2$ , a Li-Co-P system multiple oxide ( $LiCo_{0.5}P_{0.5}O_2$ ),  $LiCo_{0.4}P_{0.6}O_2$ ,  $LiCo_{0.6}P_{0.4}O_2$ . The positive electrode material which uses  $TiS_2$ , such as  $LiCo_{0.3}nickel_{0.3}P_{0.4}O_2$  and  $LiCo_{0.2}nickel_{0.2}P_{0.6}O_2$ ,  $MoS_2$ ,  $MoO_3$ , etc. as an active material can be used. Also in these, the Li-Co-P system multiple oxide which can make high especially the electromotive force and charge and discharge voltage of a rechargeable battery can use it conveniently.

[0016]In this invention, since the active material part of an anode contains Li fundamentally, what does not contain Li as an active material of the above-mentioned cathode ( $V_2O_5$ .) Although  $MnO_2$ ,  $TiS_2$ ,  $MoS_2$ ,  $MoO_3$ , etc. may be used, if the active materials ( $LiCoO_2$ ,  $LiNiO_2$ , a Li-Co-P system multiple oxide, etc.) of the cathode containing Li are used, quantity of said negative electrode active material can be lessened. Binding agents, such as polytetrafluoroethylene and polyethylene, are blended with the active material of the above-mentioned cathode for electrical conducting materials, such as acetylene black and Ketchen black, again.

[0017]As an electrolyte, the electrolysis solution and solid electrolyte in which the organic solvent was made to dissolve salts can be used. When an electrolyte is a liquid, i.e., an electrolysis solution, as these salts,  $LiClO_4$ ,  $LiBF_4$ ,  $LiPF_6$ ,  $LiAsF_6$ ,  $LiAlCl_4$ ,  $Li(CF_3SO_2)_2N$ , etc. can be used, Ethylene carbonate, propylene carbonate, dimethyl sulfoxide, Sulfolane, gamma-butyrolactone, 1,2-dimethoxyethane, N,N-dimethylformamide, It is made to dissolve in organic solvents, such as a tetrahydrofuran, 1,3-dioxolane, 2-methyltetrahydrofuran, diethylether, and these mixtures, and is prepared and used for the concentration of 0.1-3 mol/l. It is usually used for it, making a separator like porous polymer or a glass filter impregnate or fill up with this electrolysis solution. When an electrolyte is a solid electrolyte, the above-mentioned salts are mixed and used for polyethylene oxide, polyphosphazene, a polyaziridine, polyethylene sulfides, etc. these derivatives, a mixture, a complex, etc. This solid electrolyte serves as the separator of an anode and a cathode.

[0018]

[Working example]Hereafter, an embodiment is given and this invention is explained still in detail.

By embodiment 1 this example, the porous layer which consists of a Li-Si alloy is formed on a carbon layer, and the concrete manufacturing process of the anode which has this as an active material layer is shown, and it shows an example of the lithium secondary battery of the cylindrical shape further produced using this anode.

[0019][Production of an anode] On Cu tape 10 micrometers in thickness, 41 mm in width, and 300 mm in length, the organic solvent was used, the natural graphite particle with a mean particle diameter of 5 micrometers was developed, vaporization of the solvent was carried out, and the 80-micrometer-thick carbon layer was formed. However, as a binding material of natural graphite particles, it added 1weight % and PVDF was used. On this

• carbon layer, by plasma \*\*\*, the  $\text{Li}_{3.5}\text{Si}$  alloy was formed as a 5-micrometer-thick film so that porosity might be presented, and it was used as the anode (anode tape) of tape shape.

[0020][Production of a cathode] They are lithium carbonate, basic cobalt, and a phosphoric acid aqueous solution of 85% of phosphoric acid content at composition ratio (ratio of the number of constituent elements) :P Li:Co = [ After carrying out weighing of the quantity used as 2:1.5:0.5, respectively and fully mixing, ] This was put into alumina crucible, it heat-treated at 900 \*\* for 24 hours, and the quality of an oxide was manufactured. This quality of an oxide is a mixture which consists of the phosphate of lithium, an phosphate of lithium cobalt, and a cobalt oxide. This mixture was ground and the sieve adjusted to powder with a mean particle diameter of 20 micrometers. This powder 46 weight sections, acetylene black 4 weight section, the amount part of polyvinylidene fluoride duplexs, n-methyl-pyrrolidone 50 weight section was mixed, this was applied to the aluminum tape (38 mm in width, 300 mm in length, and 20 micrometers in thickness), vacuum drying was performed further, and the cathode (cathode tape) of 100-micrometer-thick tape shape was produced.

[0021][Preparation of an electrolysis solution] 1 mol/l. of lithium perchlorate was dissolved in propylene carbonate, and it was considered as electric-field liquid of a nonaqueous solution electrolyte.

[0022][An assembly of a lithium secondary battery] After having considered it as three layers on both sides of a separator made from polypropylene, having rolled this, inserting in a battery can and pouring in 3 ml of electric-field liquid on the above-mentioned anode tape and a cathode tape, connection of an electrode, sealing of a battery can, etc. were performed and a lithium secondary battery of AA (cylindrical shape) was obtained.

[0023][A charging and discharging characteristic] It has checked that service capacity of the above-mentioned lithium secondary battery and the maximum in early stages of an electromotive voltage were 500mAh and 4.5V, and were large scale and higher electromotive force. A charging and discharging cycle of stopping for 1 hour, making it charging using this lithium secondary battery until electromotive force reaches 4.2V by 100 mA of charging current, and discharging until electromotive force is set to 2.75V with the same current value as charging current, and stopping for 1 hour was repeated 50 times. Service capacity per unit weight of a cell of a service capacity maintenance factor after a charging and discharging cycle was 120 mAh/g 85%.

[0024]Li alloy which forms a porous layer of an anode in embodiment 2 Embodiment 1, A lithium secondary battery is manufactured like Embodiment 1 except having replaced with a  $\text{Li}_{3.5}\text{Si}$  alloy and having considered it as a  $\text{Li}_{1.2}\text{Zn}$  alloy. When the same charging and discharging characteristic as Embodiment 1 is investigated, service capacity of a lithium secondary battery and the maximum in early stages of an electromotive voltage 520mAh, Being able to check [ and ] that it was 4.4V and they were large scale and higher electromotive force, as for a service capacity maintenance factor after a charging and discharging cycle, 110 mAh/g and open-circuit voltage of service capacity per unit weight of a cell were 4.1V 91%.

[0025]Except having replaced with an anode tape in the comparative example 1 above-mentioned embodiment 1 or 2, and having used only 0.2 mm of metal Li foil as an anode tape, When a lithium secondary battery was manufactured like the above-mentioned embodiment and same charge-and-discharge cycle test was done, a service capacity maintenance factor after a charging and discharging cycle was 0%.

[0026]

[Effect of the Invention]As explained in full detail above, carbon shares big service capacity and the anode for lithium secondary batteries of this invention shares electromotive force generating with a porous high layer which consists of a Li alloy. By this operation, the lithium secondary battery which combines big service capacity and high electromotive force can be provided. Since the surface area of the whole anode which touches an electrolysis solution is large, Li ion can distribute and growth of a dendrite can be controlled. By this, a lithium secondary battery with little degradation by repetition of charge and discharge can be provided.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is a figure in which expanding selectively an example of the anode for lithium secondary batteries of this invention as some cells, and showing it typically.

[Explanations of letters or numerals]

A The anode for lithium secondary batteries

1 Active material layer

2 Carbon layer

3 A porous layer

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[Translation done.]

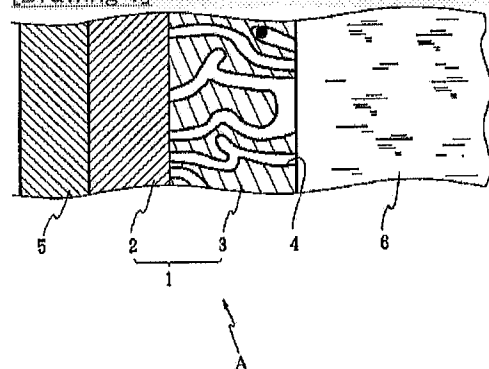
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**DRAWINGS**

[Drawing 1]



- A リチウム二次電池用負極
- 1 活物質層
- 2 カーボン層
- 3 多孔性の層

[Translation done.]